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AND REFINING:

THE EXTRACTION AND TREATMENT OF METALS

BY MEANS OF THE ELECTRIC CURRENT.

BEING THE SECOND EDITION OF

"ELEKTRO-METALLURGIE."

BY

DR. W. BORCHERS.

TRANSLATED, WITH ADDITIONS, BY

WALTER G. McMILLAN,

LECTURER ON METALLURGY IN MASON COLLEGE, BIRMINGHAM; AUTHOR OF A "TREATISE
ON ELECTRO-METALLURGY."

With 3 Plates and Numerous Illustrations in the Text.

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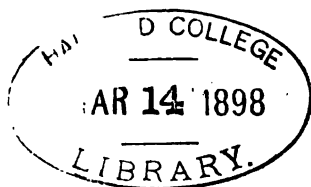
PREFACE.

IN bringing before English readers an English version of a manual so well known as that of Dr. Borchers—on a subject which has so rapidly attained to the prominent position now held by Electro-Metallurgy—but little by way of introduction is needed.

The Author, in his preface to the Second German Edition (that of 1896, from which the present volume has been translated), refers to his twelve years' practical work in chemical and metallurgical industries, and states that in preparing the first edition he had hoped to be of service to his fellow-labourers by laying before them the results of the experience with electro-metallurgical processes which he had gained in conducting experimental tests on a scale sufficiently large to enable him to form a trust-worthy opinion as to their practical value. During the four years which elapsed before the appearance of the Second Edition, electro-technology had made enormous progress; and at the end of that time the Author found himself at liberty to publish much information which previously, owing to personal considerations and business obligations, he had been prevented from giving to the world. He, therefore, re-wrote and greatly extended the work in the edition from which this version is taken.

A short sketch only is given of the newer electro-chemical theories, and the student is referred for fuller and more elaborate explanations to the works of Ostwald on General Chemistry and Electro-Chemistry, and to that of Nernst[*]

[*] Nernst's *Theoretical Chemistry from the Standpoint of Avogadro's Rule and Thermodynamics.* Translated by C. S. Palmer.

on Theoretical Chemistry. Those who are engaged in scientific or technical research are recommended to consult Ostwald's *Hand- und Hülfsbuch zur Ausführung physiko-chemischen Messungen,** and Oettel's *Anleitung zu Elektro-chemischen Versuchen.*

In the present volume, all those metals in the extraction and working of which the electric current has found any application are treated of; but electrolytic analysis, electro-plating, and electro-typing have not been touched upon. From the mass of material accumulated in journal and patent-office literature, only those papers or processes which are capable of practical application have, usually, been selected for reference. A short survey of the purely metallurgical methods of treating the metals has been added to each chapter, so that the reader may be in a position to compare such methods with electro-metallurgical processes, and to see how the two may be used in conjunction.

During the few months that have passed since the publication of the German Edition, progress has been made in many directions. The Translator has, therefore, ventured to add notes here and there in the hope of bringing the work more nearly up to date. He has also added accounts of the practical working of certain processes which have been developed since the German work was placed before the public. Extra references to English patents and the British equivalents of the metrical measurements quoted in the text have also been given. All these additions, whether in the text or in footnotes, are enclosed within square brackets, [ ], so that the reader may distinguish between the original and the supplementary matter. Tables for the conversion of certain Continental into the corresponding British units have also been added in an appendix. Whenever possible, quotations from the French have been translated direct

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* Ostwald's *Manual of Physico-Chemical Measurements.* Translated by J. Walker.

from the French text, instead of fromthe German version, and those from English sources have been reprinted *verbatim* from the original.

In arranging the additional matter, the Translator has kept in view the industrial aspect of the question, and has introduced one or two short supplementary notes referring to actual applications of processes not otherwise referred to in the text. It is believed, therefore, that under each of the various metals, separately, enough has been stated to give a good general idea of the present industrial position of that branch of the subject.

The practical applications of Electro-Metallurgy are advancing with phenomenal rapidity, especially on the Continent and in America, and there is little doubt that, if England is to hold her own in Metallurgy, she also must give more and more attention to the electro-metallurgical smelting and refining processes, which are cheapening and simplifying the work of producing high-class products abroad.

In conclusion, the translator's thanks are due to Mr. A. E. Hunt and the Institution of Civil Engineers, to the *Electrician*, and to *Industries and Iron*, for the use of the blocks employed in Figures 82A, 101A, and 50A and 50B respectively.

<div style="text-align:center">WALTER G. M^cMILLAN.</div>

METALLURGICAL DEPARTMENT,
        MASON COLLEGE,
            BIRMINGHAM, *June 8, 1897.*

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ELECTRIC SMELTING AND REFINING.

INTRODUCTION,

IN the study of electro-metallurgy we are concerned with the electrolytic and electro-thermic, rather than with the electro-magnetic, relations of electricity; and only the former two will, therefore, be treated of in this work.

ELECTROLYSIS.

Until quite recently the idea of electrolysis was associated only with those changes in the constitution of substances that could be effected by the action of electric currents generated externally. But this conception is now greatly enlarged; and the newer electro-chemistry, together with the whole fabric of chemical science, is placed upon a broader foundation, strengthened both by experimental and by mathematical investigation.

A full exposition of the modern electro-chemical theories would be out of place here, and the reader is referred for this to standard treatises, such as those of Ostwald and Nernst. A short sketch, however, of the now classical work and theories of these two writers, and those of Van't Hoff and Arrhenius, will be given before passing to the consideration of electro-metallurgical practice.

The observations of these investigators have started a new era in the science of chemistry. The fact that they, for example, afford a full explanation of the action of the voltaic cell and of the electric circuit, towards which goal science has been striving for nearly a century, points to the solidity of the basis upon which these modern theories have been founded.

Osmotic Pressure.—As the starting point for the sketch, reference may be made to the simple machine illustrated in Fig. 1, which represents a cylinder, O, partly filled with steam.

1

The steam-chamber, D, is closed by a piston, which is capable
of sliding freely in the cylinder; and above the piston is a
space free from vapour. If the piston be pressed downwards
so that the steam in the space D is compressed, and the
pressure be then wholly or in part removed, the piston will
rise in the cylinder, and the space D will be increased pro-
portionately at the expense of the empty space above, until
the internal pressure of the molecules of the vapour exactly
balances the weight of the piston or that of the load upon it,
when equilibrium will be attained and the piston will come
to rest.

Let us suppose now that the area, D, is filled with a solution
of sugar instead of with steam, and that the upper part of the

cylinder contain, waters whilst the piston is
made of a substance which allows water to
pass through it without resistance, but is
impervious to sugar. If it be true that the
laws governing the atoms or molecules of a
substance dissolved in a liquid are com-
parable with those which control the
volume and pressure of gases, the sugar
will tend to diffuse itself through the whole
of the water (to which the diaphragm of the
piston offers no resistance) until a homo-
geneous solution is obtained. But, in order
to effect this result, as sugar is unable to
traverse the diaphragm, the water in the
space above the piston will have to pass
through the latter into the area beneath it,
the piston rising as in the previous experi-
ment with compressed steam. The rising
of the piston, which is an observed fact,
points to the existence of a force tending to expand the sugar
solution under the conditions of the experiment. This force
has been termed **osmotic pressure.** Like steam pressure it
may be measured directly, and it has been determined in many
different ways.
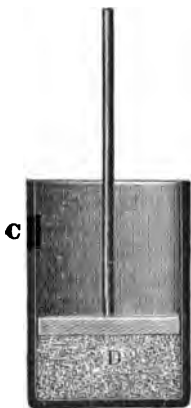
Fig. 1.

If then a solid substance be brought into contact with a
solvent, molecules of the former will pass into the latter with
a certain force—the so-called **pressure of solution**—until the
osmotic pressure of the molecules already dissolved has in-
creased sufficiently to neutralise this force and prevent any
further admission. The solution is then saturated. The
manner of solution of all solid bodies, however, is not equally
simple. But before discussing these matters more fully, it
is desirable to throw light upon some older conceptions.

Electrolytic Dissociation.—The measurement of the os-
motic pressures of various substances in aqueous solution has

led to the discovery of the remarkable fact that those substances, which for more than fifty years have been known as **conductors of the second class** or **electrolytes,** show pressures which exhibit no agreement with those calculated from their molecular weights in the gaseous condition, and from the concentration in the solution. This irregularity was only brought into agreement with the theory of Van't Hoff, when Arrhenius adduced evidence that, on solution, the molecules of such substances were dissociated into free but opposing electric **ions.** To enunciate a theory in such direct opposition to the hitherto accepted (and still widely held) views on chemical affinity was bold, but proofs were not wanting. Indeed, before Arrhenius had published his work on electrolytic dissociation, Ostwald, working in the same direction, had collected so much material available for proof that the new theory was immediately placed upon a firm basis.

It is true that, as the publications of Hittorf and Kohlrausch show, these same ions had long been regarded as the carriers of electricity, hydrogen and the metals **(cations)** being considered as carrying positive electricity, and the acid radicles **(anions)** as carrying negative electricity; but the conception that they existed in the solution in the free state was not understood, and, indeed, was contrary to the chemical teaching of the day. But according to the newly advanced theory, an aqueous solution, for example, of common salt contains free sodium-ions and free chlorine-ions; a solution of caustic soda contains free sodium- and free hydroxyl-ions; and one of sulphuric acid free hydrogen- and sulphur tetroxide-ions.

Theory of Electrolysis.—The sum of all the charges of positive and negative electricity of the various ions in an electrolyte at rest is *nil;* and the ions themselves are the carriers of electricity. If one may picture the anions and cations uniformly distributed through the solution, and each ion charged with a definite quantity of electricity, clinging to it with a certain force, it will be evident that a transfer of electricity—and, therefore, the production of an electric current —can only be effected when the ions are so set in motion that they can give up their electrical charges to, or take them from, certain surfaces in the electrodes. *Electric currents in conductors of the second class, and movement of the ions are, therefore, two quite inseparable conceptions, just as in mechanics and energetics force and motion cannot be imagined apart from one another.* The **conductance of electrolytes** is, therefore, governed by the degree of electrolytic dissociation (the number of free ions) in the solution, and by the rapidity of motion and the electrical charge-capacity **(valency)** of the ions.

For the conduction of electrical charges to or from the ions, it is usual to introduce into the solution containing them at least

two conductors of the first class (metallic conductors) as poles
or electrodes, which must not be in actual contact with one
another at any point within the liquid.

In order that a substance may exist in the ionic condition, it
is necessary that its ions shall carry certain definite electrical
charges. As soon, then, as they are caused to give up their
charges they cease to be ions, and separate in the neutral or
molecular condition at the point where the discharge has been
effected, unless, of course, they should take part in further
chemical changes or secondary reactions. The discharge points
for the cations are the cathodes, those for the anions anodes.
To produce a migration of the ions—and, therefore, a continuous
electric current—care must be taken to impart constant negative
charges to the cathode, in order to neutralise the positive
charges of the cations with which it is bombarded, whilst at the
same time the anode must be maintained positively charged, so
that the negative charges of the anions may be annulled.

On the other hand—and this brings us back to the considera-
tion of the solution pressure—the substances which we have
learned to recognise as constituents of an electrolyte can only
pass from the molecular to the ionic condition when the ions
have the opportunity of receiving their full electrical charges.
For example, to bring about the solution of a metal it is not
alone sufficient that its tension of solution shall be high and the
osmotic pressure of its ions low. Metals, hydrogen included,
pass into the ionic condition at the moment of solution in the
electrolyte, and they must, therefore, be so placed that each ion
may at that instant receive the charge of positive electricity
which is necessary to its independent existence as a cation.
Since the anodes are caused to receive charges of positive
electricity in order that they may neutralise the negative charges
of the anions, they clearly afford the surfaces from which newly
formed metallic ions may derive their positive charges. Hence,
the anodes should be the places at which metals are dissolved;
and this is entirely in harmony with the well-known practice of
electro-metallurgy.

The pressure with which a substance capable of forming ions
tends to cause those ions to pass into solution is known as the
electrolytic solution pressure. If this pressure be very
great a substance may, under certain circumstances, require no
expenditure of electrical energy from outside sources to bring it
into solution, because it is capable of withdrawing the charges
necessary for its own ions from those of others—*e.g.*, hydrogen
or metallic ions—already present in the solution. The ion from
which a charge has been thus seized separates in the neutral
condition ; and so, unless some secondary reaction take place, it
follows that the solution of those metals, which exert a high electro-
lytic pressure, is always attended by an evolution of hydrogen, or

by the separation of another metal. The excess of the electrolytic pressure of a dissolving material over the osmotic pressure of the ions present in the solution can be determined experimentally. It constitutes the **electromotive force** which sets the ions in motion, and, therefore, produces the current in galvanic batteries. If, in any mechanism, a strong force be applied at one end of a moving part, whilst there is a weak opposing force at the other end, this end may either be moved from its position with a velocity depending upon the excess pressure, or it can itself exert a force equal to the difference between those applied at the two ends. In elements of the Daniell type, for example, zinc forms the anode, copper sulphate is the electrolyte, and copper the cathode. The positive charges required for the dissolving zinc ions are derived from the copper ions existing in the solution; that is to say, the charge of the copper ions is transferred to the zinc anode by the quickest (though not always by the shortest) route, through the metallic connections outside the solution. The copper ions are, therefore, withdrawn from the solution at a definite rate, which depends upon the excess of the electrolytic solution pressure of the zinc over the osmotic pressure of the copper ions, and their charges are, therefore, impelled, under a certain perfectly definite pressure, through the conductors which join the poles of the battery. This pressure can be estimated by introducing known resistances into the electric circuit, the energy of the electro-chemical machine, like that of any other, being determined by the addition of a load (brake); and a difference of pressure or potential is thus measured between two places, one of high and the other of lower pressure. The result of this measurement, and, therefore, the difference of pressure, is known as the **potential.** *

To return to the example of the Daniell cell. If the metallic

* The unit of potential is the volt. A volt is the difference of pressure shown at the ends of a resistance of 1 ohm through which a current strength of 1 ampere is passing.

An (International or Board of Trade) ohm is equal to the resistance of a column of mercury 1063 mm. long, and 1 sq. mm. in cross section.

A coulomb is the quantity of electricity which will deposit 1·118129 mg. of silver, or the equivalent amount of other substances, from their respective solutions.

An ampere, the unit of current strength, is equal to a coulomb per second, and, therefore, represents the quantity of electricity which is capable of neutralising that of the above weight of ion per second. A current of 1 ampere also liberates 10·436 c.c. of mixed hydrogen and oxygen per minute, when passed through a water voltameter.

At the ends of a simple conductor of 1 ohm resistance, through which a current of 1 ampere is flowing, there will be a difference of potential equal to 1 volt; and the following relation exists between current strength (C), difference of potential (E), and resistance (R) :—

$$C = \frac{E}{R}$$

connection between the anode and cathode be broken, then (since in a properly constructed cell there should be no copper ions in the immediate neighbourhood of the zinc anode) the solution immediately surrounding the anode will become charged with negative electricity, owing to the absorption of positive electricity by zinc ions; and thus the anode will also become negatively charged by contact, which will effectually prevent any further formation of zinc ions. At the cathode the reverse takes place; the cations are prevented from imparting to it further positive charges, owing to the accumulation upon it of positive electricity from previous cations. The migration of the ions, therefore, comes to a standstill. This condition, which is known as polarisation, can be produced in other ways :—By the chemical alteration of electrodes or electrolytes through the action of deposited ions; by changes of concentration in the electrolyte; or by electro-thermal effects at the points of contact between electrode and electrolyte.

Conditions of Electrolysis.—From the foregoing considerations, the following conditions may be deduced as favourable, both to the production of the maximum current, and to the most complete utilisation of electrical energy from external sources in an electrolytic cell :—

1. At any electrode from which substances are required to pass into the solution in the form of ions, the opposing osmotic pressure in the solution from ions of the substance to be dissolved must be as low as possible; the concentration of the electrolyte solution at this point should, therefore, be low.

2. At an electrode on which a substance is to be deposited, on the contrary, the osmotic pressure of the ions to be separated out, and the concentration of the solution, should both be as high as possible.

3. The substance to be dissolved, which is, therefore, passing into the ionic condition, must be provided freely with the electrical charges necessary for its ions.

4. The charges of those ions which are being withdrawn must be rapidly and completely removed.

The first two points are sufficiently clear, but unfortunately they can seldom, if ever, be simultaneously satisfied in metallurgical practice; for example, in the refining of metals the material which is dissolved from the anode has to be re-deposited upon the cathode. The ideal conditions of concentration for the electrolytes are clearly prescribed by conditions 1 and 2, viz. :—Wherever it is possible, salts of the metal to be deposited should be present in concentrated solution around the cathodes, but should be absent from the liquid surrounding the anodes. Technically, however, the fulfilment of these conditions is usually surrounded with difficulties. It may be desired, for example, so to alter the construction of an electrolyte cell for antimony

deposition with 21 anodes and 20 cathodes that it may satisfy the above demands. It would be impossible to gain the desired end without using 21 diaphragms, and thus introducing complications quite independent of those involved in the management of the solution. The increased difficulty in the construction and working of the necessary apparatus, especially in the case of large electrolytic installations, has so many disadvantages that it far outweighs any gain which would result from the use of a plant designed on theoretically perfect lines. It is customary, therefore, to use as strong a solution as possible in the single-compartment vats, which are universally employed, whilst any detrimental alterations of concentration at the electrodes are avoided by a brisk circulation of the liquid, produced, if necessary, by a current of air. There are, however, quite exceptional cases, in which the success of the whole process depends upon the quantity of the salt existing in solution in the bath. As an example of this, reference may be made to Bunsen's experiments with chromium.[*] He writes that "a not less important consideration is the relative proportion of the constituents of the electrolyte which is to be submitted to the current. If, for example, the quantity of chromium chloride in the solution be gradually increased, the strength of the current and surface area of the electrode remaining constant, a point is soon reached at which the separation of chromium sesquioxide is accompanied by a reduction of the metal, and at last is completely replaced by it."

To turn now to conditions 3 and 4, the metallurgist by empirical methods has already gained that knowledge of the correct method of operation, which Nernst has indicated upon theoretical grounds. In copper refining, for example, the copper contained in the crude copper anode is dissolved at that pole, and is re-deposited on the cathode, copper sulphate being used as the electrolyte. For this purpose the two poles are connected in a circuit in which a dynamo-electric machine is included. Thus when the dynamo imparts positive electrical charges of low potential to the anode, the copper ions cause an increase in the osmotic pressure of the solution, and, migrating through the liquid, produce an immediate separation of copper on the cathode. The positive electrical charges of the copper ions separated at the cathode are conducted through the outside circuit back to the anode. Hence, as is demonstrated by actual practice, only a small pressure or electromotive force is necessary to effect the transfer of large quantities of copper. And scarcely any better example is needed to show that not only the atoms of metal, but their electrical charges with them, are carried through the solution from the anode to the cathode.

* *Poggendorf's Annalen,* 1854, vol. xci., p. 619.

In spite of the apparently opposite characters of the galvanic battery and the electrolytic cell, the one producing and the other utilising electric currents, they are really identical in their internal action, since in both the transport of electricity is effected by means of the moving ions. *This transport of electricity, by the agency of migrating ions, combined either with the conversion of neutral substances into ions, or* vice versâ, *or with the alteration of the charge capacity or valency of the ions themselves,* constitutes the phenomenon known as **electrolysis.**

Relation of Current Strength to Weight of Deposit.— The statement that every ion is capable of receiving and transporting a perfectly definite charge of electricity has already been often repeated. Electrical energy is, therefore, associated with a definite mass of weighable matter; and the correctness of this assertion was proved by Faraday more than sixty years ago. Faraday's fundamental law of electrolysis requires in fact only to be translated into the language of the newer electro-chemistry to make it harmonise entirely with modern views. Ostwald's translation of this law is as follows :—

The transfer of electricity in electrolytes results only from a simultaneous transfer of ions, and in such a manner that like quantities of electricity are translated along with chemically equivalent quantities of the various ions.

Hence, as Ostwald goes on to show, *equivalent weights of various ions have equal capacities for electrical energy.*

After the explanations already given, no further explanation of this law should be necessary. Some of its practical consequences are included in the following table (p. 9). The quantities by weight of various substances which, in their ionic condition, can transport 1 unit (coulomb) of electricity are termed the **electro-chemical equivalents** of those substances. They are identical in weight with the amounts of the same substances that would be deposited from electrolytes by a current of 1 ampere in 1 second (that is, by 1 coulomb), or that would be dissolved and pass into the ionic condition under the same conditions of current and time.

The following table shows the electro-chemical equivalents of the elements most frequently met with, together with the valency, the atomic weight, and the nature of the electrolyte for which the figures are calculated. The last column but one shows the weight of each substance in kilogrammes that would be deposited by a current of 736 amperes in the space of one hour ; [and the last column gives the English equivalent of this—viz., the weight in lbs. per hour per 746 amperes]. The use of these last two series of numbers will be gathered from the succeeding remarks.

Name of Element.	Nature of Electrolyte.	Atomic Weight, O = 16.	Symbol and Valency.	Electro-Chemical Equivalent in Milligrammes.	Weight Deposited by Current of 736 Amperes per hour.	Weight Deposited by Current of 746 Amperes per hour.
					Kilogram.	Lb.
Aluminium.	Oxides and salts.	27·08	Al. III.	0·093541	0·247846	0·554
Antimony.	Sulpho-salts.	120·34	Sb. III.	0·415361	1·100540	2·459
Arsenic.	Arsenites.	75·00	As. III.	0·258975	0·686180	1·533
Barium.	Haloid salts.	137·04	Ba. II.	0·709798	1·880680	4·202
Bismuth.	Oxide salts.	208·01	Bi. III.	0·718258	1·903096	4·252
Bromine.	Bromides.	79·96	Br. I.	0·828336	2·194759	4·904
Cadmium.	Salts.	112·08	Cd. II.	0·580518	1·538140	3·437
Calcium.	Haloid salts.	40·00	Ca. II.	0·207180	0·548944	1·227
Chlorine.	Chlorides.	35·45	Cl. I.	0·367257	0·973084	2·174
Chromium.	Chromous salts.	} 52·15 {	Cr. II.	0·270105	0·715670	1·599
„	Chromic salts.		Cr. III.	0·180070	0·477113	1·066
Cobalt.	Cobaltous salts.	59·55	Co. II.	0·308479	0·817347	1·826
Copper.	Cuprous salts.	} 63·44 {	Cu. I.	0·657175	1·741248	3·891
„	Cupric salts.		Cu. II.	0·328587	0·870624	1·946
Fluorine.	Fluorides.	18·99	F. I.	0·196727	0·521247	1·165
Gold.	Haloid salts.	197·25	Au. III.	0·681104	1·804653	4·032
Hydrogen.	Water or acids.	1·003	H. I.	0·010392	0·027534	0·062
Iodine.	Iodides.	126·86	I. I.	1·314184	3·482061	7·780
Iron.	Ferrous salts.	} 56·00 {	Fe. II.	0·290052	0·768521	1·717
„	Ferric salts.		Fe. III.	0·193368	0·512348	1·145
Lead.	Oxides and oxide salts.	206·91	Pb. II.	1·071695	2·839562	6·345
Lithium.	Haloid salts.	7·03	Li. I.	0·072823	0·192951	0·431
Magnesium.	Haloid salts.	24·37	Mg. II.	0·126276	0·334580	0·748
Manganese.	Manganous salts.	55·09	Mn. II.	0·285338	0·756031	1·689
Mercury.	Mercurous salts.	} 200·4 {	Hg. I.	2·075943	5·500421	12·291
„	Mercuric salts.		Hg. II.	1·037972	2·750210	6·145
Nickel.	Nickelous salts.	58·88	Ni. II.	0·305009	0·808153	1·806
Oxygen.	Oxides.	16	O. II.	0·082872	0·219577	0·491
Platinum.	Haloid salts.	194·83	Pt. IV.	0·504560	1·336882	2·987
Potassium.	Haloid salts.	39·14	K. I.	0·405409	1·074171	2·400
Silver.	Salts.	107·94	Ag. I.	1·118129	2·962594	6·620
Sodium.	Haloid salts.	23·06	Na. I.	0·238857	0·632875	1·414
Strontium.	Haloid salts.	87·52	Sr. II.	0·453309	1·201087	2·684
Sulphur.	Sulphides.	32·06	S. II.	0·166070	0·440019	0·983
Tin.	Stannous salts.	} 118·10 {	Sn. II.	0·611699	1·620755	3·622
„	Stannic salts or stannates.		Sn. IV.	0·305849	0·810377	1·811
Tungsten.	Oxide compounds.	} 184 {	W. III.	0·635352	1·683428	3·761
„	Tungstates.		W. VI.	0·317676	0·841714	1·881
Zinc.	Salts.	65·38	Zn. II.	0·338635	0·897247	2·005

Valency.— This table is intended primarily for practical use. It is to be observed that many of the metals quoted in the table have two equivalent numbers. For example, for the transport of 1 coulomb of electricity, in copper solutions, there will be necessary either 0·657175 mg. or 0·328587 mg.

of copper, according as a cuprous or a cupric salt of copper is employed as electrolyte. Thus whilst a cuprous compound will give a deposit of 0·657175 mg. of copper in a second with a current strength of 1 ampere, a cupric compound under the same condition will give only half that weight. Hence, the same material may have a different **charge-capacity** or **valency** under different circumstances. But since it is well known that the material may be easily converted from one form of combination to the other—for cuprous salts may be oxidised and cupric salts reduced—it is evident that the charge-capacity of the ions, and, therefore, the valency of the metal, is variable.

Concerning the practical use of the table, it will suffice to add some remarks upon the numbers given in the last column.

Relation of Work Expended to Weight of Deposit.—
The unit of mechanical power is the horse-power (H.P.), corresponding to an expenditure of work equal to 76 kilogramme-metres per second. Since 1 volt × 1 ampere (= 1 watt) of electrical work is equivalent to a quantity of heat represented by 0·24 gramme-unit of heat, and this in turn is equivalent to 0·102 kilogramme-metre of mechanical work, 1 horse-power is evidently equivalent to an electrical expenditure of 746* watts (volt × ampere).

If now the available power of a dynamo in horse-power units be represented by the symbol I.H.P.; the efficiency of the dynamo, which for machines of medium size is 0·8, by s; and the electromotive force required for a given electrolytic process, as found experimentally, by V; and, finally, if the number in the last column of the table be represented by w; the weight, W, of the material that should be yielded per hour in return for the specified expenditure of power may be found from the following equation :—

$$W = \frac{\text{I.H.P.} \times s \times w}{V} \text{(in lbs.).†}$$

Current-density.—Bunsen begins the opening of one of his celebrated electro-metallurgical theses with the words: "*The density of the current used for electrolysis* (that is to say, the relation of current volume to electrode area) *exerts the most important influence on its chemical effect*; for the power of the current to overcome (chemical) affinities increases with this density."

In electro-metallurgy the cathode is chiefly considered in determining the current-density that would be suitable in any given case, for it is here that the separation of metal takes place;

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* [This is the English horse-power; in the original text the German unit is given, which is equivalent to 75 kilogramme-metres per second, or 736 watts.—TRANSLATOR.]

† [By substituting the foreign H.P. for I.H.P., and the number in the last column but one for w, the result is obtained in kgs., as given in the original work.—TRANSLATOR.]

and the success of the whole process often depends on the fulfilment of the requirement that the metal shall be obtained in coherent plates of sufficient thickness, which shall not require to be melted or otherwise treated subsequently. Whenever possible, the area of the anode is made to exceed that of the cathode; then, the cathode-surface remaining constant, the difference of potential in the bath may be reduced to any fixed limit by increasing the anode area. The current-density at the anode will thus be lower than that at the cathode. In the electrolysis of fused substances this condition cannot always be observed, especially if the containing vessel itself be employed as cathode; but the substances deposited at the anode are in these cases nearly always gaseous (chlorine, oxygen, or carbonic oxide), so that they rapidly rise to the surface and escape. No general rule can be laid down for the selection of a suitable current-density. But the electromotive force necessary for any given electrolytic process should be calculated, and then the metal should be deposited by a current of which the potential does not vary greatly from this amount. . The current-density at the cathode determined by this electromotive force will always be correct, provided that the metal deposited has the desired properties.

Calculation of Potential.—For full details of calculations to determine the electromotive force required in an electrolytic process, reference should be made to the text-books named above. For use in metallurgical practice, and in the research laboratories connected with works, the formulæ hitherto employed are not in all cases suitable since, as Nernst himself points out, only those circuits in which liquids alone are employed to the exclusion of metals have at present been studied in full detail. For the electro-deposition of metals such calculations are rarely made, the chief desideratum being the extraction of the required metal in a directly utilisable form. This difficulty has caused the failure of many theoretically good processes; and even the most accurate calculation can only afford values which approximate the real requirements. But these are imperfections inseparable from the comparatively crude methods of work required in practice; and they will in no wise detract from the services of Nernst, who has given so clear an insight into the phenomena of electrolysis.

Formulæ for the calculation of approximate values have been determined as follows :—One coulomb (ampere-second) deposits 0·010359 multiplied by a milligramme-equivalent (or 0·000010359 times a gramme-equivalent) of any substance. A gramme-equivalent of any ion carries, therefore, a charge of 96,537 coulombs. If the ion should be set in motion by an electromotive force, E (in volts), an expenditure of work equivalent to 96,537 × E joules is effected. Since the work of 1 joule (= 1 volt-coulomb) is equal to the energy which an acceleration of 1 metre in a

second is able to impart to a mass of 1 kilogramme (and is therefore equivalent to $\dfrac{1}{9\cdot81} = 0\cdot102$ kilogramme-metre), it corresponds to 0·00024 kilogramme-calorie, or 0·24 gramme-calorie, 425 kilogramme-metres being equivalent of 1 kilogramme-calorie.

The heat of decomposition (H) of a gramme-equivalent of various substances would, therefore, correspond to a heat quantity of 0·24 × 0·96537 × E gramme-calorie. From this equation H = 0·24 × 0·96537 × E is obtained

$$E = \frac{H}{0\cdot24 \times 96537} = \frac{H}{23169}$$

If the usual heat of formation of a compound be taken, this number may be substituted for H ; but then the fraction must be divided by the number (n) representing the valency of the ions contained in the solution ; therefore

$$E = \frac{H}{n \times 23169}$$

ELECTRO-THERMIC WORK.

The heat evolved by a current of 1 ampere in traversing a resistance of 1 ohm amounts to 0·24 gramme-calorie per second ; and to produce a current of 1 ampere in a resistance of 1 ohm, a fall of potential of 1 volt is necessary. The heat-equivalent of 1 watt (1 volt-ampere) is therefore 0·24 gramme-calorie, so that an electric horse-power (746 volt-amperes) affords 0·179 kilogramme-calorie per second. Given, then, a known power (I.H.P.) in horse-power, the heat obtainable from it, H (in kilogramme-calories), in the external electric circuit is

$$H = 0\cdot179 \times \text{I.H.P.} \times \varepsilon_m \times \varepsilon_t \times \varepsilon_d$$

if the efficiencies of the motor, of transmission, and of the dynamo, respectively be represented by the symbols ε_m, ε_t, and ε_d.

With a given current strength, C (in amperes), and a known resistance, R (in ohms), the heat h (in gramme-calories) obtainable in t seconds can be determined by the following formula of Joule's :—

$$h = 0\cdot24 \times C^2 \times R \times t.$$

From the numbers so obtained, and from the weight and the specific heat of the substance which affords the resistance, the approximate temperature obtainable may be determined with ease, especially if the duration of the electric heating be short. The materials for further calculation are to be found in electro-technical hand-books and publications, incorporated in numerous tables of the electrical properties of the more important materials.

The heating effect of the electric current has become, in electro-metallurgy, of scarcely less importance than the chemical; and in effecting the more difficult reactions, the advantages of the electrical heating process, as compared with those utilising the heat of combustion, must be manifest.

The limit of temperature that may be reached by electro-thermic processes is at least 2,000° C. above the highest attainable by combustion, and may be taken at about 4,000° C. To reach this temperature, only the purest carbon blocks may be used as conductors and resistances for the current, and even these begin to be converted into vapour at about 4,000°.

The desired temperature is produced by the conversion of electric energy into heat either within the substance to be heated, or in other substances placed in immediate contact with it. For this purpose, if the material to be treated be a con-ductor, it is introduced as a resistance into the electric circuit; otherwise it is placed in intimate contact with a suitable resistance. Substances fusible or reducible with difficulty may be thus treated even in vessels made of a non-refractory material, or of one which, if raised to the full temperature of the furnace, would exert a prejudicial influence upon the chemical reactions taking place within. By heating-methods of this character, the author has succeeded in proving that *every oxide* is capable of being reduced *by means of carbon.*

A further great advantage in the use of electric furnaces is the possibility of a rapid and almost instantaneous heating to the required temperature, and of an equally rapid regulation of the heat applied. Finally, it may be noted that the electric heating of a substance may readily be conducted *in vacuo*, or in any required atmosphere, so that the chemical action of particular gases may be excluded or applied at will.

[The Cost of Electro-metallurgical Work.—This is ob-viously one of the points upon which it is most difficult to generalise. It is characteristic of "applied science" that apparatus and methods must be modified to suit local con-ditions; and there must be an elasticity of detail in an indus-trial process, that is often under-estimated by those who have never come into touch with practical work. But if the process itself be subject to variation, the cost is even more so; for this depends partly upon the special modification of the process that is adopted (which is, of course, governed to a large extent by the same local conditions that influence the cost); partly upon the charges for supervision, and for labour, skilled and otherwise; partly upon the situation of the works, their proximity to the raw material and to sources of power, and the expense of transport both for plant, materials, and finished product; partly upon the nature of the power used, and upon the way in which it is applied; and partly upon the size of

the installation, and the continuity with which it is run. If steam-power be used, the local cost of the fuel per heat unit, and other minor considerations connected with the behaviour of the fuel during combustion, must be known; and if water power be available, the cost of damming, diverting, controlling, and utilising the water must be taken into account, together with the rental of the fall, and the possibility of climatic interruptions to the continuity of the process. All these conditions are so variable under different circumstances that it is impossible to give any generally applicable estimate of cost.

In generating electricity by steam-power, it has been found that in electric-lighting stations, a Board of Trade unit of electricity (that is, 1,000 watt-hours or 1 kilowatt-hour) may be produced with good triple-expansion engines for 1⅛d. This sum is equal to 1⅛d. per electrical H.P., and includes such indirect charges as management, interest, and depreciation, &c. In very large lighting installations the cost has been reduced considerably below this figure; and there is no doubt that with continuous working it should be very far below it. It must be remembered that in electric light stations the work is very intermittent, and the average proportion of the capacity of the plant actually used is rarely in excess of 20 per cent., even when calculated upon the whole year, and that these conditions are most unfavourable to economy. The annual cost of each H.P., if calculated on the basis of 1⅛d. per E.H.P.-hour for 365 × 24 hours would amount to a little over £41. A very small plant, even if worked continuously, might, it is true, give an equally unfavourable result, but with a large plant run continuously, such as would be used in electro-metallurgical installations, it should not exceed one-third, and under favourable circumstances it may be less than one-fourth, this amount.

Emery[*] has estimated as follows the cost of running a 250-H.P. compound condensing engine, requiring 18 lbs. of water per I.H.P., assuming an evaporation of 8½ lbs. of water per lb. of coal, with coal at 12s. 6d. per ton :—

Cost of coal per net H.P. . . .	= 0·173d.	
Labour (in manufacturing districts) .	= 0·085d.	
Supplies and ordinary repairs †. .	= 0·045d.	
		0·303d.
Sinking fund, taxes, and insurance (at 5 per cent. on total cost) . .	= 0·052d.	
Interest on capital (at 5 per cent. on total cost)	= 0·052d.	
		0·104d.
Total cost per net H.P. . =		0·407d.

[*] *Electrician*, 1896, vol. xxxviii., p. 9. The original estimate is given in dollars and cents; for purposes of calculation, these have been reckoned at 4s. 2d. and ½d. respectively.

† This charge is based on observation.

This estimate is apparently made out, however, upon the basis of a 3,080-hour year (or 10 hours a day for 308 days); if run continuously the above cost works out to

$$(365 \times 24 \times 0.407)d. = £14, 17s.,$$

as the cost of each H.P. per annum. In the latter case all the items would be smaller than those given in the estimate, and the annual cost of each H.P. should therefore fall proportionately below £14, 17s. With a triple-expansion engine of 500 H.P., using every care, the cost of a net H.P. hour is estimated at 0·35d. per hour, or (less than) £12, 15s. per annum on continuous running. It will thus be seen that continuous work and the use of a high percentage of the load for which the generators were designed are most favourable to economy, and hence to the application of power to electro-metallurgical work.

The cost of water-power is very variable. Emery (*loc. cit.*) states that it has been developed in America for from £1, 13s. to £2, 10s. per H.P.-year; but that in a plant on the Merrimac, mainly owing to high rent-charges, it has cost £6, 5s. per annum. The cost at Schaffhausen is taken at £2, 10s. per H.P.-year. It is a somewhat common fallacy to assert that water-power may be had for nothing, but the capital outlay upon an installation for utilising it may be very considerable, and in some cases might be almost prohibitive; and, as Swinburne has pointed out, it is probable that in the course of a few years the commercial value of waterfalls will become better known, higher rents will be demanded, and the balance in favour of water as compared with steam-power will then be reduced almost to a vanishing point.

There are to be seen in America electro-metallurgical works using steam in successful competition with others run by water-power. Hence, although streams and falls will naturally be utilised as fully as possible, there is little doubt that steam will be more than able to hold its own in this field, more especially, if advantage be taken of the waste power that is superabundantly available in many districts. The outlook for electro-metallurgy is therefore bright. Very many electric smelting and refining processes have already displaced the older and more costly and cumbrous metallurgical methods, as the following pages will show, and every year brings fresh victories in the same field.—TRANSLATOR.]

PART I.—ALKALI- AND ALKALINE EARTH METALS.

For electro-metallurgical purposes it is convenient to adopt a system of grouping somewhat different from that which may be considered as purely chemical. Classified according to analogies in the methods of production, these metals would be included in the following groups :—

> First Group.—Magnesium, Lithium, Beryllium.
> Second   ,,   Sodium, Potassium.
> Third   ,,   Calcium, Strontium, Barium.

FIRST GROUP.—MAGNESIUM, LITHIUM, BERYLLIUM.

CHAPTER I.

MAGNESIUM.

Properties of the Metal.—Magnesium (Mg, Atomic weight $= 24$; specific gravity $= 1.75$) is a white lustrous metal with a fibrous crystalline structure; it is so far malleable that it may be rolled into wire or ribbon, but by reason of its relatively low toughness it can readily be reduced by filing to a fine powder, a property which greatly favours the use of the metal in pyrotechny. It melts at a temperature of 500° to 600° C., and boils at temperatures exceeding 1,100° C. Large and thick pieces of the metal are but little altered by exposure to the air, although they may become superficially oxidised, especially in the presence of moisture; they may even be melted in an open crucible without risk of burning. In the form of a fine powder or thin plate, however, magnesium oxidises very readily, and at a higher temperature it burns with a brilliant light, which is particularly rich in the chemically active rays. The powdered metal also,

when once moistened, cannot be dried without undergoing complete oxidation. At the ordinary temperature it readily decomposes water which contains even a small proportion of dissolved salts, but it has less effect on pure water. Finely divided magnesium burns freely in superheated steam, in sulphur, and in the halogens. The metal dissolves readily in most acids and salts; in the latter case it either displaces the metal which the salts contained previously, or it forms basic compounds with the salts themselves. The heat of formation of magnesium compounds is so great [Mg + O = MgO (146,100)] that the metal is able to liberate not only other metals, but even metalloids, from their compounds, so that, for example, carbonic oxide, carbon dioxide, silica, and boron trioxide are reduced by it, with separation of carbon, silicon, and boron respectively.

Occurrence in Nature.—It is evident, therefore, that magnesium cannot occur in the free state in nature. It is found in the form of salts; as a haloid salt in carnallite ($MgCl_2 . KCl . 6H_2O$) and kainite ($MgCl_2 . MgSO_4 . K_2SO_4 . 6H_2O$); as sulphate in kieserite ($MgSO_4 . H_2O$); as carbonate in magnesite ($MgCO_3$) and dolomite ($MgCO_3 . nCaCO_3$); as silicate, always in combination with other silicates, in asbestos, steatite, serpentine, talc, meerschaum, and many other minerals. Of all these minerals carnallite is alone employed as a source of metallic magnesium.

Early Experiments in Reduction.—If one may judge from Davy's account of the properties of the metal that he obtained, it seems improbable that his experiments in the reduction of magnesia * by means of potassium vapour at a white heat actually yielded magnesium. Bussy,† Buff,‡ and Liebig, § however, obtained the pure metal by decomposing the chloride with potassium, and thus imitating Wöhler's method of reducing aluminium.

Bunsen's Electrolytic Reduction Process.—Bunsen was the first to recognise the possibility of decomposing fused magnesium chloride by electrolysis, and to indicate the manner in which other metallic chlorides or halogen compounds in the fused and anhydrous condition might also be decomposed into metal and halogen. In 1852 he published a note‖ on this subject, of which the following is a translation :—"Fused magnesium chloride is so easily decomposed by the current, that several grammes of heavy metallic regulus may be obtained from it in a short time with the aid of a few carbon-zinc elements.

"The magnesium chloride is best prepared by Liebig's well-known method. For the decomposing cell it is convenient to

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* *Phil. Trans.*, London, 1808, p. 336.
† *Journ. de Chim. médicale*, 1849, vol. vi., p. 141.
‡ *Pogg. Ann.*, vol. xviii., p. 140.
§ *Pogg. Ann.*, vol. xix., p. 137.
‖ *Liebig's Ann.*, 1852, vol. lxxxii., p. 137.

use a porcelain crucible (Fig. 2) about 3½ in. high and 2 in. wide, divided into two compartments by a diaphragm, reaching from the top half way to the bottom ; in one of these the liberated chlorine escapes upwards, and is thus prevented from obtaining access to the magnesium deposited in the other.   The diaphragm may conveniently be made from a thin porcelain cover, broken to the required shape with the aid of the notches of a key.   The crucible is covered with a lid made of ordinary fire tile, filed into shape, and bored with two holes (Fig. 3) through which the poles are passed.   These poles are cut out of the material from which the battery carbons are prepared, a process that presents no difficulty, as such carbons may easily be bored, turned on the lathe, filed, or even provided with a screw thread.   The carbon poles are fastened to the cover by means of the wedges *d, d,* which are also of carbon, and which serve to grip the platinum strips that are used to convey the current to and from the

Fig. 2.—Bunsen's
electrolyte cell.

Fig. 3.—Bunsen's
carbon electrode.

apparatus.   The saw-like notches in the negative pole are provided to retain the reduced metal which collects in them in the form of regulus.   In the absence of this arrangement, the metal would float to the top of the relatively heavier liquid and would there be at least partially burned.   In conducting the experiment, the crucible, with the cover and the poles attached, to it, are first heated until they are red hot, they are next filled to the brim with fused magnesium chloride, and the electric circuit is then completed."

Bunsen quotes by way of example an experiment in which the current from 10 carbon-zinc elements was allowed to operate for 115 minutes.   From the measurements that were made at intervals of five minutes, he calculated the theoretical quantity of reduced magnesium at 4·096 grammes, which would correspond to a current of 4·7 amperes.   Since no details are given of the size and arrangement of the battery cells, it is impossible to ascertain what electromotive force was used for the decomposition in this experiment.

Matthiessen's Double-Chloride Process.—Matthiessen's proposal [*] to substitute the double-chloride of magnesium and potassium (carnallite) for the single magnesium chloride, which is with difficulty obtained anhydrous, is especially worthy of notice, as it has been adopted at a later date for the production of magnesium on a manufacturing scale.

Berthaut's Process.—Berthaut's patented process [†] consisted in the use of a soluble anode made by compressing a mixture of carbon and magnesia, and employing it in a bath of magnesium chloride. This was an imitation of Deville's proposal [‡] to use an anode composed of aluminium and carbon for the reduction of aluminium. Electrodes of this description, however, are liable to
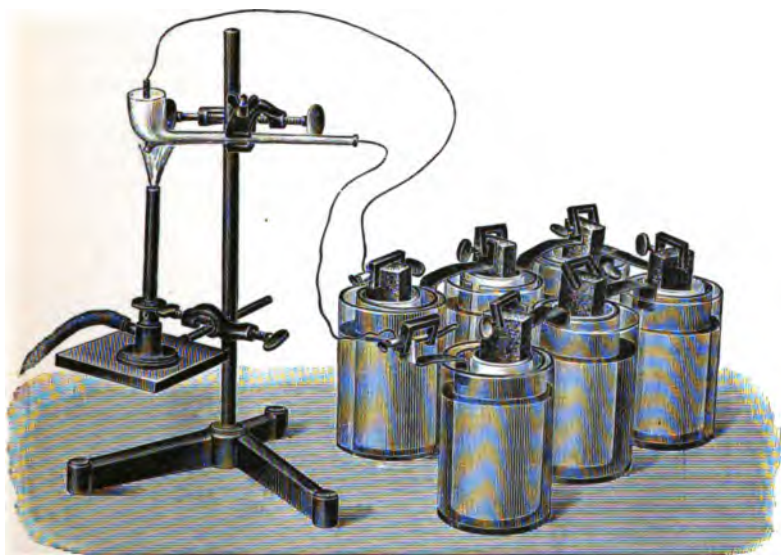
Fig. 4.—Gorup-Besanez apparatus.

crumble up owing to the extraction of the oxide, and thus to contaminate the bath. This disadvantage was understood by Le Chatelier,[‡] who sought to overcome it by enclosing the anodes in porous cells. Although Deville's and Le Chatelier's inventions were primarily intended to be applied to aluminium reduction, they are equally available in the extraction of magnesium, as Berthaut has recognised, for he has included the reduction of both these metals in his patent, and has adopted Deville's proposal as his own invention. Everyone, however, who has experimented with electrodes of this description has

[*] *Journ. Chem. Soc.*, vol. viii., p. 107.
[†] Eng. Patent 4087, of 1879.   [‡] See *Aluminium*.

become convinced of their uselessness. Although the idea is undoubtedly sound, it has not been possible to carry it into effect owing to technical difficulties that are practically insurmountable.

Small-scale Apparatus.—A very simple apparatus for lecture experiments has been described by v. Gorup-Besanez :[*] a clay pipe is supported in a holder (Fig. 4), and the bowl is filled with the double-chloride of magnesium and potassium, which is then melted with the aid of a Bunsen burner. A knitting-needle is now introduced through the stem until it comes into contact with the fused salt. The needle being connected outside with the negative pole of a battery forms the cathode ; a fragment of coke connected with the other pole and dipped into the bowl of the pipe from above serves as anode. After cooling, small globules of magnesium are to be found distributed through the solidified mass of salt; but the greater part of the magnesium reduced in this experiment is burned.

Fischer's Apparatus.—Apparatus of the type suggested by F. Fischer[†] in 1882 for the electrolysis of carnallite is not well adapted to the reduction of magnesium. Fig. 5 shows a long-
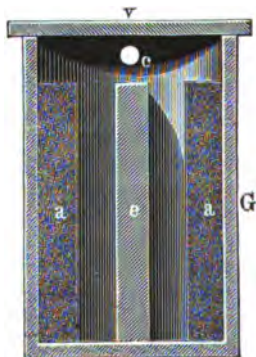
Fig. 5.—Fischer's earliest magnesium reduction apparatus.
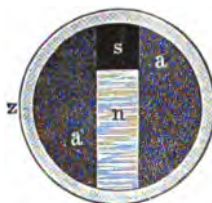
Fig. 6.—Fischer's continuous electrolysis apparatus.

shaped vessel, G, made of graphite or magnesia, in which the magnesium chloride of the carnallite is decomposed by a powerful electric current that passes through the positive carbon plates a placed on each of the long sides, and the negative pole e placed between them. Throughout the experiment a current of reducing gas is passed through c to prevent the re-combination of the reduced magnesium with the liberated chlorine in the upper part of the vessel. The mixture of gases makes its escape partly

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[*] *Lehrbuch der anorganischen Chem.*, vol. iv., p. 517 (Gorup-Besanez).
[†] *Dingler's Polytechnisches Journ.*, 1882, vol. ccxlvi., p. 28.

through the crevice between the crucible and the cover v, and partly through a tube provided at the opposite end of the cell. F. Fischer attempted to evolve a continuous system of electrolysis by causing the melted double salt to flow through a series of porcelain tubes, z, (Fig. 6), arranged in succession in a suitable furnace, and provided with electrodes, a, consisting of halfround carbon plates, between which the fused salt, n, flowed one way, and a current of gas, s, in the opposite direction. In each of these forms of apparatus the major part of the separated magnesium would be burned by the chlorine, which is produced simultaneously, before the protecting influence of the reducing gases could come into play. Fischer accordingly replaced this
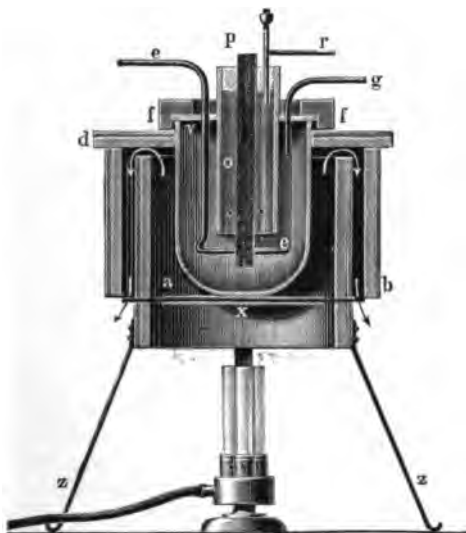
Fig. 7. —Fischer's later apparatus.

apparatus very shortly afterwards by another of more practical construction.[*] In this case the porcelain crucible (from the Royal porcelain factory in Berlin) was enclosed within two cylinders, a and b, made of sheet iron lined with asbestos (Fig. 7), bound by three strong wires beneath, and supported on three feet, z. The object of the rings was to equalise the temperature, so that the crucible might be steadily and uniformly raised to a clear red heat. The cover, d, was also coated on the under side with asbestos, and had an opening through which the crucible might easily pass, in order that it should rest upon a thick iron wire, protected from the action of the flame by a pipe-clay tube,

* Wagner-Fischer, *Jahresbericht der Chem. Techn.*, 1884, p. 1317.

x. The hot gases from the three burners circulated evenly around the crucible inasmuch as they were afterwards compelled to pass downwards between *a* and *b* in the direction indicated by the arrows. As soon as the double salt was melted, a circular asbestos plate, *v*, was placed upon the crucible, and pressed into close contact with the rim by a heavy cast-iron ring, *f.* Passing through the asbestos cover was a clay tube, *o* (made by removing the bottom from a porous battery-cell), in the side of which a few holes were bored. Through the clay tube there were passed both the carbon, which served as positive electrode, and a small tube provided with a side connection, *r*, for the removal of chlorine. These were kept in place by means of asbestos plates. This form of tube was chosen in order to facilitate the removal of accidental obstructions, and to enable the operator, after raising the stopper, to test for the evolution of chlorine by the application of a strip of litmus paper. A length of iron wire, *e*, 5 mm. thick, served as the negative pole, and had its lower end bent into a ring so as to encircle the carbon. A very gentle current of reducing or neutral gas, previously dried by passing over calcium chloride, was introduced through the tube *g*, and made its escape along with the chlorine through *r*. When coal gas was used, the hydrogen and hydrocarbons present in it combined with the chlorine.

The electric current was derived from a dynamo built by Uppenborn and Gackenholz, and capable of affording a current of about 50 amperes at from 9 to 10 volts; and the dynamo was driven by a 1-H.P gas engine made by Körting, of Hanover. When one crucible was employed, the current strength averaged 35 amperes; but by coupling two crucibles in series, it ranged from 22 to 25 amperes, which was equivalent to from 44 to 50 amperes in the two together, and the hourly out-turn of magnesium amounted to 10 grammes [154 grains.] The metal was deposited in the form of a slime upon the negative electrode, but melted at a clear red heat into globules of the size of a nut which slowly rose to the surface. Instead of the iron ring *e*, a carbon plate may be used as cathode, and from this the globules of magnesium detach themselves more readily than they do from the former. By this method the reduction of magnesium may readily be made the subject of a lecture experiment.

Magnesium may be produced conveniently enough in Fischer's apparatus, but the decomposing cell has the disadvantage of being very fragile. For lecture and laboratory purposes the apparatus is certainly useful; but in no case is it adapted for regular use on a large scale, as one would suppose it to be from the account given in Wagner-Fischer's *Handbuch der Chemischen Technologie* (edition 1893), where it is the only form described.

Graetzel's Apparatus.—A short time before the publication of the above process, Graetzel's patent* was taken out. This

* German Patent, 26,962, 1883.

patent, which has been described very frequently, was a combination of several ideas. The following account is taken from the specification :—

"The present improvements in apparatus for the electrolytic production of the alkaline earth metals on a manufacturing
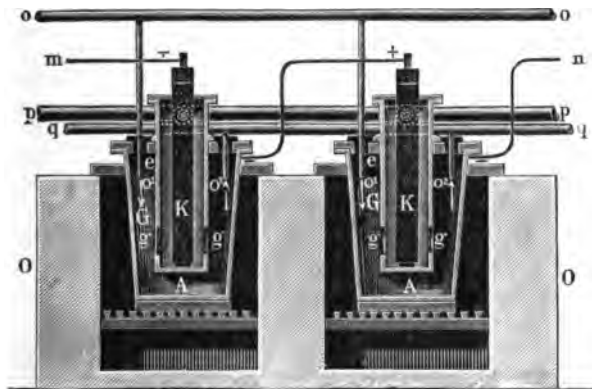
Fig. 8.—Graetzel's apparatus.
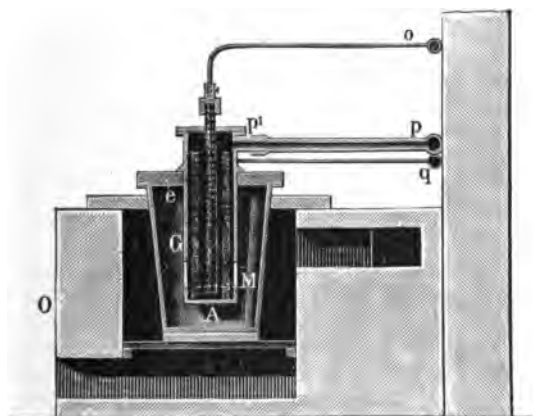
Fig. 9.—Graetzel's apparatus.

scale from their respective chlorine and fluorine compounds, with the subsidiary assistance of a current of reducing gas, consist, on the one hand, in the use of the melting vessel itself as the negative electrode, and, on the other hand, in the separation of the two electrodes in such a way that the chlorine produced at the positive electrode can be carried off separately

from the reducing gases. A dynamo is employed as the source of electricity."

Of the accompanying illustrations, Figs. 8 and 9 show the longitudinal and the cross sections respectively of the apparatus as used for the production of magnesium; Fig. 11 gives a longitudinal section of the plant arranged for producing aluminium; whilst Fig. 10 is a view of the inner vessel, G.

The melting vessels, A, which also serve as electrolyte cells, are set in the furnace, O, each in its own hearth; they may be arranged either in parallel circuit or in series, and range from two to five in number, according to the strength of current available. The vessels, A, which may have any desired form, but are most conveniently crucible-shaped, are made of metal, and are used as negative electrodes; those intended for aluminium reduction are of copper, iron, or steel, and those for

Fig. 10.   Fig. 11.
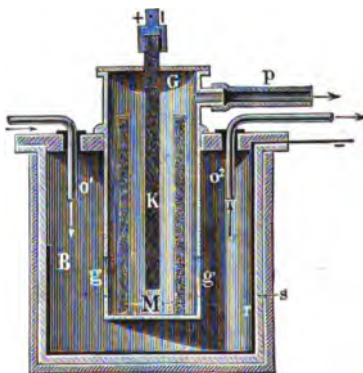
Graetzel's apparatus.

magnesium of malleable cast steel. Each stands upon a fire-brick plate placed in the middle of a grate, and the furnace is closed by means of a fire-brick cover, divided into two halves, and shaped to suit the disposition of the melting vessel.

Each melting vessel is provided with a lid, $e, e,$ of the same metal as the vessel itself, and the reducing gases are led into it from the main, o, through the tube o^1, and are afterwards conducted away through o^2 into the return main, q.

In order to insulate the electrodes and to keep the chlorine (which is evolved in K) separate from the reducing gas, the carbon electrode is enclosed in a special vessel, G, which is suspended within the crucible, A, through an opening in its cover, e. This vessel, G, is made of fireclay, porcelain, or other fire-resisting material, which must at the same time be a non-conductor of electricity, and is preferably cylindrical

In shape. It is closed above with a cover, through which the carbon electrode is passed, whilst at the bottom or on its sides it is provided with perforations, g, which serve to give the melted charge free access to the carbon anode. The chlorine generated in G escapes through a side tube, p^1, at the top of the compartment into the chlorine main p, which, like the mains o and q, serves all the crucibles in the installation. The coupling of several melting vessels with one battery is effected in the usual manner, as indicated in the illustrations, where m and n represent the connections with the dynamo.

For the reduction of aluminium the arrangement of the apparatus is somewhat modified. This metal tends to sink to the bottom of the melting vessel, and so to come into contact with the negative electrode, which should, therefore, consist of a separate metallic conductor (preferably of aluminium) independent of, and inserted within, the crucible. Accordingly, the crucible, s (Fig. 11), is made of porcelain or stoneware, or of some other refractory material of a similar nature, and is protected from direct contact with the flame by an outer sheathing of metal. The metallic conductor r, placed within s, is connected to the negative pole of the dynamo. If preferred, the cathode-cell may be introduced into a graphite crucible instead of into a porcelain vessel, in which case the outer metallic sheath may be omitted; or it may be used in conjunction with a metallic vessel, which must, of course, be capable of resisting the heat to be applied.

In order to lessen the internal resistance of the apparatus, and, at the same time, to enrich the bath as the supply of electrolyte becomes exhausted, the plates or rods, M, which consist of a mixture of alumina and carbon for the reduction of aluminium, or of magnesia and carbon for that of magnesium, are introduced into the compartment, G, parallel with the carbon electrode, but quite independent of it. The carbon combines with the oxygen of the oxide in these rods, and thus enables the metal previously combined with the oxygen to unite with the chlorine that is present in the compartment.

The following claims are made in this patent specification :—
1. An apparatus for the production on a manufacturing scale of the earth metals from their anhydrous chlorine and fluorine compounds, consisting of a closed metallic melting vessel, A, which serves also as the negative electrode, with inlet and outlet for reducing gas, in combination with the non-conducting and fire-resisting vessel, G, which surrounds the positive electrode, K, and is provided with openings in the sides or at the bottom, to insulate the electrodes from one another, and to facilitate the separate removal of the halogen produced. 2. In the manufacture of aluminium on a large scale in the above-described manner, the use of metallic conductors, especially of aluminium,

introduced into the melting vessel as negative electrodes, as described with reference to Fig. 11.   3. To diminish the electric resistance within the apparatus first described, as well as for the enrichment of the smelting bath as it becomes impoverished, the use of plates or rods, M (Figs. 9 and 11), of alumina and carbon, or of magnesia and carbon, in equivalent quantities respectively, which should be placed within the vessel, G, independently of the electrode.

The only *actual novelty* in the whole patent was the *introduction* of the plates or rods of magnesia and carbon, or of alumina and carbon, to be used in the production of magnesium and aluminium respectively, and this has not proved successful; its use was discontinued in the aluminium and magnesium factory at Bremen even at the time that Graetzel was managing the works. The effect of these plates, like that of Deville's oxide-carbon anodes, was only to introduce impurities into the bath, and thus to cause irregularity and inconvenience in the working. In order to bring about the desired reaction, as formulated in the equation

$$MgO + C + Cl_2 = MgCl_2 + CO$$
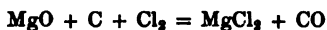
the temperature of the bath would have to be maintained much higher than is desirable either for the production of magnesium, for the preservation of the apparatus, or for preventing the destruction of the plates themselves through the removal of the oxide.

The *introduction of reducing gases* into the cathode chamber was made a prominent claim in the specification.   But this proposal had been made a year earlier by F. Fischer, as we have seen above.   Hiller[*] also had arranged for the use of a reducing atmosphere in the cathode chamber of his apparatus for the reduction of strontium and lithium.   Moreover, this precautionary measure is entirely unnecessary in the electrolysis of carnallite. Practically the whole of the magnesium remains adhering to the immersed electrode and to the walls of the crucible, provided that a current of suitable strength be used and that the fused salt be not connected up with the battery until it has been melted sufficiently long, and at a sufficiently high temperature, to drive off the last traces of water, which are retained by it with the most obstinate pertinacity.   The use of reducing gas is not, therefore, necessary on this account; but if the crucible be immersed in the fire almost to the top rim it will be found that in the absence of reducing gases the walls of the vessel become strongly corroded above the level of the fused mass within.   This is due to the metal of the crucible becoming chloridised, owing to the combined effects of the hot fire-gases without and the acid-gases within, the latter being always present above the surface of

[*] F. Hiller, *Lehrbuch der Chemie*, 1863.

carnallite when it is melted in the presence of even a small proportion of air. The crucible walls, therefore, above the level of the fusion become rapidly corroded through, whilst, in addition, the melted carnallite tends to creep over the rim of the vessel on to the outer surface, and there, aided by the furnace gases, it exerts a most destructive influence. This action may, however, be prevented by adopting the construction of crucible used by Borchers. This crucible (Fig. 12) is provided, at a distance of about 2 to 2½ in. from the top, with a flange, which serves to support it with its lower portion immersed in the fire. The upper part of the crucible being thus exposed freely to the air remains sufficiently cool to reduce to a minimum both the formation of acid gases and the corrosion of the vessel. Thus the furnace gases come in contact only with those portions of the crucible walls which are in contact with fused substance within, and which serve as cathode surfaces. The tendency of the melted salts to creep up the side of the crucible is completely pre-

Fig. 12.—Borchers' flanged crucible for electrolytic reduction.

vented because, even if the uppermost margin of the fused mass within the crucible should not be crystallised in contact with the comparatively cool walls, yet any thin layer of fused salt that might reach above this level would be at once solidified.

Finally, the use of the melting vessel as cathode, claimed by Graetzel as his invention, was anticipated in actual practice by Davy so long ago as the year 1808.

Napier's Electrolytic Vessel.—An account may be given here of an apparatus patented by Napier* in 1844. It was originally intended for the extraction of copper, but, as in the case of Graetzel's and other apparatus, several elements may be treated in it.

Napier used a large crucible or other convenient vessel made of some conducting material, of which the inner side, with the exception of the bottom, was lined with a coating of clay. The copper ore, roasted as free as possible from sulphur, was mixed with the necessary fluxes and fused in the crucible; the melted mass was then submitted to the action of the galvanic current in such a way that the crucible itself formed the cathode, whilst the anode was an iron rod united to a plate at the lower end. It is thus clear that even in 1844 an apparatus for the reduction of metals had been patented,† which consisted of a melting vessel

* English Patents 10,362, 1844, and 684, 1845. *Cf.* Houston, *Journ. Franklin Inst.*, 1889, vol. cxxv., p. 376.

† *Cf.* Graetzel's Patent claims, pp. 23, 25.

made of some conducting material and serving as the negative electrode, in combination with a non-conducting and fire-resisting vessel, open at the bottom, and surrounding the positive electrode for the purpose of insulating the electrodes and facilitating the removal of the anion.

Borchers' Magnesium Process.—In accordance with the principles explained above, and following the pattern of Troost's*
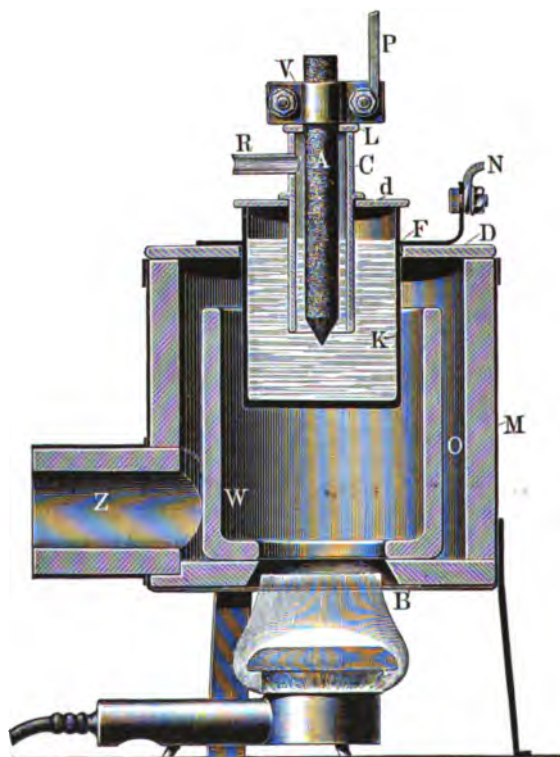
Fig. 13.—Borchers' experimental furnace for the electrolysis of fused salts.

apparatus, the cell surrounding the carbon electrode being reduced in size, whilst at the same time taking into account the experience which led to the adoption of the shape of crucible depicted in Fig. 13, the author has designed an apparatus suitable for a large number of experiments in the electrolysis of fused salts. Within the iron crucible, K, which forms the cathode, is suspended the carbon rod, A, as anode, surrounded by the porcelain

* See p. 34.

tube, C. The anode is connected to the conducting wire from the dynamo by means of the screw clamp, V, and is supported by the ring-shaped porcelain cover, L, whilst the porcelain tube rests by means of a collar on another annular porcelain plate, d; the weight of the whole crucible is in turn borne by the fire-brick cover, D, of a Perrot furnace, upon which it is held by the flange, F; and this, by an extension on one side, makes electrical connection with the negative pole of the dynamo through the binding screw, N. The furnace consists of a wide fire-clay cylinder, O, protected externally by a sheet-iron jacket, M, which may be supported either by feet attached to it, or by a temporary stand; and the whole is closed beneath by a fireclay plate, B, provided with a central opening. The internal fireclay cylinder, W, serves to convey the heated gases from a sufficiently powerful gas-burner, first of all upwards and around the crucible, and thence downwards through the annular space between W and O to the flue, Z.

In using the apparatus, the empty crucible and its appurtenances should first be heated for a considerable time, while the carnallite is being melted, preferably, in a second crucible. During the heating of the former, a piece of charcoal may be placed in the crucible to prevent the oxidation of the inner surface, which should be perfectly clean, and to minimise the loss of anode material by combustion; but the charcoal must of course be removed before introducing the melted salt.

During electrolysis at a dull red heat (about 700° C.), the magnesium deposits upon the walls of the vessel in globules, which rapidly increase in size, while the chlorine, mounting upwards through C, finds an escape by the side tube, R.

Working with a current density of at least 1000 amperes per square metre [0·64 ampere per sq. in.] of cathode surface, the current density at the surface of the anode will amount to about ten times as much, even if an unusually thick carbon rod be employed. In spite of this, an electromotive force of only 7 to 8 volts is required, which may be reduced to 1 to 2 volts (where an economical installation is sought) by increasing the size of the anode.

After continuing the electrolysis for a sufficiently long time, an inspection of the contents of the crucible through the clear fused salt will show when the required quantity of metal has been accumulated. The current is then broken, the screw connections are unfastened, and the cover, d, together with all that it supports, is removed from the melting vessel. The flame is now somewhat increased, and the mass of metal clinging to the walls is detached with the aid of an iron scraper shaped to correspond with the inner surface of the crucible. The whole contents of the vessel are then poured into a flat box made of sheet iron, which must be cold and perfectly dry, and any metal

that still adheres to the walls of the vessel must be rapidly scraped off. The solidified melt, after cooling, is broken up, and the globules of magnesium are picked out. The larger pure shot may be melted together without flux in a plumbago crucible, but the less pure metal must be fused and refined by a process which will be described later.

The apparatus just described may be used for operations on a manufacturing scale almost without any alteration other than that necessitated by the proportional enlargement of the various parts. Under these circumstances it will only be necessary to

Scale, 1 : 20.
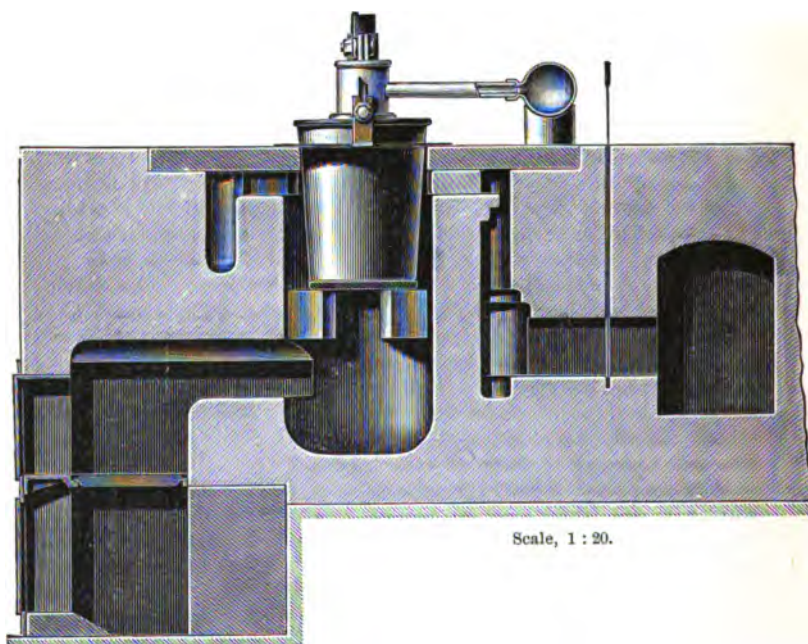
Fig. 14.—Borchers' furnace for the manufacture of magnesium.

discuss briefly the special points to be observed in the use of a plant of this nature.

After the above description, Fig. 14 requires no further explanation, so far, at least, as concerns the various parts of the apparatus. In a plant of about twenty times the size of the figure the melting vessel and its appurtenances are suitable to the application of a current of 250 to 300 amperes, which corresponds to an outturn of 0·199 to 0·238 kg. [0·44 to 0·5 lb.] of magnesium per hour. It is not advisable to use an apparatus much larger than that which is here figured, not

only for structural reasons, but on account both of the size of the electrodes that would be required and of the distance between them. It is preferable to use a greater number of vessels of ordinary size connected up in series; but in that case the crucibles must be supported in separate furnaces, in order to avoid short-circuiting between them through the deposition of soot or other conducting material. Several melting vessels, however, may be served with fuel from a single generator. The grate, whether gas-firing or solid fuel be used, is best built in a separate chamber, so that the crucible may be protected from the direct action of the flame (but little extra heat is required during the actual progress of electrolysis), and that the fluid contents of a leaky crucible may be prevented from flowing into the fuel. To facilitate the removal of such material a small collecting-chamber may be provided beneath the crucible, as shown in the illustration.

It is necessary to arrange for a heating-chamber, in which spare porcelain or clay portions of the apparatus may be kept hot, so that damaged parts may be replaced without loss of time. This chamber is conveniently heated by the waste gases from the furnace.

Concerning the manner of conducting the process and the emptying of the melting vessel, sufficient has been said already on p. 29. The necessity for lifting apparatus, transporting cranes and the like, for use with this larger plant, requires no further mention.

Melting of Electro-deposited Magnesium.—The larger and purer pieces of magnesium may be melted together in a crucible in an ordinary fire, but the less pure and the fine-grained material must always be submitted to a refining operation. For this purpose carnallite is melted in an iron crucible, and the crude magnesium is thrown into the fused mass. At a dull red heat an iron rod is introduced, and with its aid the metal lying at the bottom of the crucible is as far as possible pressed into one mass. The temperature is now gradually raised to that of a bright red heat, until a point is reached at which the specific gravity of the magnesium is less than that of the flux. The metal then, liquating from its impurities, floats to the surface in the form of globules of considerable size, and is removed in perforated sieve-like ladles. The surface-tension of melted magnesium is so great that the metal cannot flow through the fine perforations of the ladle, although the flux may thus be drained completely away. The purified metal is finally melted together in an iron crucible to separate the last traces of slag, and to enable it to be cast into the bars or rods required for the market.

Electro-thermic Reduction of Magnesium.—Knöfler and Ledderboge* have proposed to smelt magnesium by placing a

* German Patent 49,329, Feb. 6, 1889.

mixture of carbon and magnesia in the form of rods in an electric circuit after the manner of carbons in an arc-lamp; the magnesium and carbonic oxide thus produced were to be prevented from reacting with one another, either by the introduction of reducing gases or by conducting the whole experiment *in vacuo*. The process would probably be workable, but it is questionable whether it would be successful financially. The considerable electromotive force required for the operation, the high price of the magnesium-unit in pure magnesia as compared with carnallite, the circumstance that magnesium is volatile at temperatures even lower than that required for the decomposition of the oxide, and the difficulty of condensing the resulting metallic vapour from its admixture with carbon monoxide and other gases, are sufficient grounds for predicting the practical failure of the process.

Applications of Magnesium.—The use of magnesium remains restricted, and the hopes, at first entertained, that it might be utilised in the manufacture of aluminium have remained unfulfilled, owing to the introduction of more advantageous methods for the latter purpose ; its employment, however, as the source of a powerful light in pyrotechny and photography is by no means inconsiderable. The price of magnesium, as compared with that of aluminium (at the present time) and the alkali metals, especially sodium, has led to its introduction into the chemical industries only in very limited quantities, in spite of its high reducing power. It is, however, especially well suited to the dehydration of alcohols, ethers, and oils, because the hydroxide formed by its reaction with water is quite insoluble in most of these substances. If it be still employed in melting nickel to remove the last traces of oxide dissolved in the metal, it is less on account of its reducing properties, which it possesses in common with aluminium, than because any excess of magnesium that may be added does not alloy with the nickel. Magnesium is also recommended for the refining of other metals, such as copper, German silver, and steel, being added to effect the removal of small quantities of dissolved oxides, sulphides, and phosphides. In laboratories it is employed as a powerful and reliable reducing agent.

The aluminium and magnesium work at Hemelingen, near Bremen, is at present the only factory producing the latter metal.

CHAPTER II.

LITHIUM.

Properties of the Metal.—Lithium (Li; atomic weight = 7; specific gravity = 0·5936) is a soft metal belonging to the alkali group. Surfaces of the metal protected from the air have a white silver-like lustre. It melts at 180° C., and has been vaporised by Troost at a clear red heat (about 1000° C.). At temperatures below 200° C. it may be melted in the air without taking fire, but at higher temperatures it bursts into flame, emitting a blinding white light, and becoming converted into oxide with the evolution of much heat. It unites with sulphur and the halogens under similar circumstances, evolving both light and heat. It decomposes water at the ordinary temperature, and floats to the surface where, unlike the other alkali metals, it remains tranquil, without enkindling either itself or the hydrogen produced by the reaction. It is obvious that the action of acids must be very energetic upon a metal such as lithium, which is able to decompose water, and whose salts are soluble, almost without exception.

Occurrence of Lithium in Nature.—Of the compounds of lithium which occur in nature, the chloride is found in many mineral waters; a fluoride together with a silicate is met with in lepidolite and a phosphate in triphylite. Numerous other minerals, together with a few plants (*e.g.*, tobacco), also contain lithium, but even the richest minerals never contain more than 4 per cent. of this metal, and usually only from 1·5 to 2 per cent.

Extraction of Lithium.—The many methods proposed for the treatment of these minerals are so far alike that the lithium is in all cases rendered soluble by converting it into the sulphate or chloride. As a natural result of this treatment, it follows that in addition to more easily separable metals, the alkali and alkaline earth metals, which are always present, must pass into solution with the lithium, and the separation of these latter salts at present introduces great difficulties, and adds considerably to the cost of the process. Such an operation is, however, unnecessary if it be intended to produce metallic lithium, because this metal may be completely separated in a perfectly pure condition and with the greatest ease (in the absence of mag-

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nesium salts) by electrolysing a fused mixture of alkaline and alkaline earth chlorides. Bunsen and Matthiessen in 1854, working with lithium chloride, showed that the successful electrolysis of fused alkaline chloride was quite possible; and the former* wrote as follows on this point :—"The lithium chloride is melted in a small thick-walled porcelain crucible by means of a Berzelius lamp, and is then treated with the current from 4 to 6 zinc-carbon elements. The current is passed through the fused chloride from a pointed fragment of gas carbon to a piece of iron wire the thickness of a knitting needle. Even after the lapse of a few seconds a molten silvery-white regulus is seen to be forming upon and clinging to the immersed portion of the wire; and within two and a-half to three minutes it will have grown to the size of a small pea. The metal is obtained, with the aid of a small spoon, by raising the melted regulus out of the solution, together with the wire electrode; and as this operation may be repeated at intervals of three minutes, it is an easy matter to reduce an ounce of lithium chloride in quite a short time."

Fig. 15.

Troost's apparatus for the electrolysis of fused lithium chloride.

Troost's Process.—The publication of Bunsen's results led naturally to further work in the same direction. In publishing his confirmation of these results, Troost, in 1856, described a modified apparatus which, in view of the patent claims advanced by later inventors, is worthy of special attention. A cast-iron crucible, T (Fig. 15), 4¾ inches high and 2 inches wide at the mouth, was used as the melting vessel. This was covered by a close-fitting lid, D, provided with two perforations, one of which was 0·2 inch wide, and served to admit the negative pole, K; whilst through the other, which was 1¼ inches in diameter, there was passed a sheet metal cylinder, having an internal diameter of 1·14 inches, and reaching downwards to half the depth of the crucible. Within the metal cylinder was a porcelain tube forming a sheath for the positive pole, A, and a means of escape for the separated chlorine. The lithium gradually accumulated at the negative pole, and the apparatus could be left to itself for an hour at a time, provided only that the decomposed chloride was replaced from time to time, as re-

* *Liebig's Ann.*, 1855, vol. xciv., p. 107.

† *Comptes Rendus*, 1856, vol. xliii., p. 921; and *Ann. de Chim et de Phys.*, 1856, vol. li., p. 112.

quired, by the introduction of fresh salt through the porcelain tube.

According to the author's experience with apparatus of the kind just described, lithium and other metallic chlorides may be electrolysed in them for a short time. Even, however, if the negative electrode be initially insulated from the iron cover and crucible, the separated metal floats to the surface and makes electrical connection with the crucible and the sheet-iron tube, so that all the iron portions of the apparatus which are below the level of the fused salt soon form part of the negative pole. So far as the separation of lithium is concerned, this action is in itself harmless; but, unfortunately, the metal becomes deposited on the inner side of the sheet-iron tube, and as lithium very readily attacks both silica and alumina, the porcelain tube with which the metal is now in contact is so attacked that it is soon rendered porous, and the inner surface of the iron then becomes the principal seat of reduction for the lithium. The result of this is that the electrodes are insufficiently separated, and short-circuiting is brought about through the porous substance of the porcelain tube. Such an apparatus may not, therefore, be used continuously for any length of time. There can be no doubt that in the arrangement, as Troost described it, the crucible either acted as the negative pole from the very beginning of the electrolysis (for Troost does not mention that it was insulated from the cathode wire), or, if it were insulated at first, that it did so within a very short time afterwards, for the reduced metal rapidly accumulates upon the surface of the fusion in sufficient quantity to bridge over the space between it and the original wire pole.

Accordingly in 1856, we find Troost * using " for the production of metals from their anhydrous chlorine compounds, a closed metallic vessel, which serves also as negative electrode, in combination with a non-conducting and fire-resisting vessel, which is open at the bottom, and surrounds the positive electrode, with the object of separating the two electrodes and of conducting away the chlorine produced."

Hiller's Apparatus.—Hiller† has described an apparatus for the production of strontium, that is especially well adapted to the extraction of lithium from its chloride.

In Fig. 16, t is a porcelain crucible which contains the fused lithium chloride. The cathode consists of an iron wire, of which the end, k, is enclosed in the bowl of a clay tobacco-pipe, p. The lithium separates at k, and, being specifically lighter than the fused chloride, collects upon the surface of the liquid in the pipe-bowl, which protects it completely from the re-oxidation that would otherwise result from contact with the air. It is

* Compare Graetzel's claims in his patent specification, on pp. 23, 25.
† F. Hiller, *Lehrbuch der Chemie*, 1863.

advisable, before commencing the electrolysis, to remove the air from the pipe. To effect this, a glass tube, *g*, is attached to the pipe-stem by means of a perforated cork ; beyond this is a narrow glass tube, *d*, leading to a caoutchouc tube, *e*. The second glass tube is fitted to the first with the aid of a cork at *c*, and between this cork and the outer tube is passed the iron electrode wire. The wire is wound several times around the small glass tube at *d*, and when the end, *k*, has been adjusted in the centre of the pipe-bowl, the whole arrangement is held firmly in position by covering the joint, *c*, with a paste of plaster of Paris. The air in the pipe is displaced by passing a current of perfectly dry hydrogen through the caoutchouc tube, *e* ; the bowl of the pipe is then dipped into the fused chloride, the caoutchouc
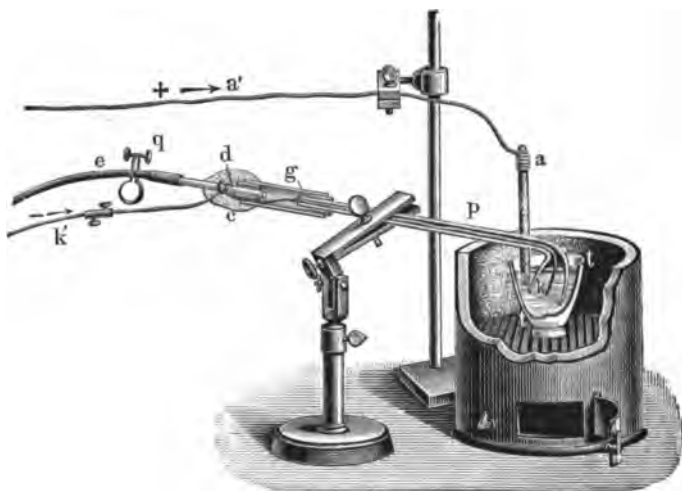
Fig. 16.—Hiller's apparatus for the extraction of strontium.

tube is disconnected from the hydrogen generator, the bowl is sunk into the chloride to the depth indicated in the figure, and the rubber tube is finally closed with a pinch-cock, *q*. It would, however, be still simpler to substitute hydrocarbon vapour for hydrogen ; to this end it would only be necessary to introduce some paraffin into the upper part of the pipe-bowl. On immersing the bowl in the melted salt, the paraffin would vaporise and drive out the air before it through the caoutchouc tube, *e*, which could then be closed by the clamp as before. In order to prevent the contact of the separated lithium with the walls of the pipe, which would lead to the contamination of the metal with silicon, the inner side of the bowl is coated with a thin layer of graphite, The graphite is first made into a thick paste by stirring it well

with a dilute solution of lithium chloride; the paste is then painted over the surface of the pipe-bowl, and after it has become thoroughly air-dried, the whole is heated to a red heat. The anode, a, consists of a gas-carbon rod connected to an iron wire, a'. From 3 to 4 Bunsen's cells are sufficient for the electrolysis. As soon as the circuit is completed decomposition sets in, which may be recognised by the copious evolution of chlorine at the anode; and it is now only necessary to see that the lithium chloride remains in a state of fusion. At the end of an hour the current may be interrupted, and the fire drawn from the grate; then, after cooling completely, the crucible and pipe may be broken, and a regulus of lithium will be found surrounding the iron wire.

Although this apparatus might easily be made on a larger scale, and although it represents a distinct advance towards the economical electrolysis of alkaline chlorides, yet it does not satisfy all the requirements of a profitable installation.

Grabau's Apparatus. — The electrode cell, patented by Grabau[*] for use in the extraction of metals of low specific
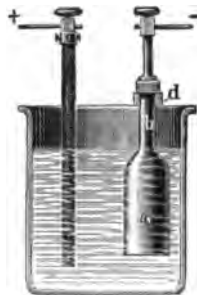
Fig. 17.   Fig. 18.

Grabau's electrode cell for use with light metals.

gravity, may here be described on account of its similarity to the last-named apparatus. The bell-shaped cell, a (Figs. 17 and 18), is suspended by the stem, b, from the transverse support d, and is provided with the pole, f, which terminates at the highest point of the inner surface of the bell. The cell, a, is closed above, but it is open below, and should be quite immersed in the bath. Either by a siphon-shaped tube, or otherwise, the air initially present is given a passage for escape so that the bell may be completely filled with the fused material. The metal separates on the pole, f. But this apparatus cannot be used for an extended operation, for there is no non-conducting material known that will, under these circumstances, afford resistance for any

[*] German Patent 41,494, 1887.

length of time to the action of the alkali metals in the presence of fused alkali chlorides. Even a few hours will suffice to bring about the perforation of strong and thick porcelain tubes by the alkali metals, in consequence of the reduction of the silicates by them.

Guntz's Process.—A notable ignorance of past work in practical electro-chemistry was shown by Guntz,[*] who, in December, 1893, presented to the French Academy the description of a process, from which the following account is taken:—A mixture of 200 to 300 grammes of potassium and lithium chloride in equal proportions (fusing point 450° C.) is melted over an ordinary Bunsen-burner. When fusion is complete the electrodes are introduced. The anode consists of a carbon rod 8 mm. in diameter, the cathode of an iron wire about 3 to 4 mm. thick. The latter is enclosed within a glass tube 20 mm. wide. After applying a current of 20 volts and 10 amperes for *about an hour* there will be found in the glass tube a fluid column of lithium, which stands at a level of more than 1 cm. above that of the fused salt. To obtain the metal the electrodes are separated, the glass tube is raised out of the liquid, and the fluid lithium which floats upon the surface of the melt is removed with the aid of an iron spoon and poured into a dry ingot mould. All this, however, had been accomplished 30 years previously, only the earlier experimenters had been more economical of electric energy, of which they had used but one-fourth part of that employed by Guntz.

As it has already been shown, the conditions required for the extraction of lithium are of the simplest, as compared with those to be observed in the case of the better-known alkali metals.

Treatment of Lithium Minerals.—In the treatment of lithium minerals, a solution is first obtained which contains only the chlorides of the alkali and alkaline earth metals. This solution is then evaporated to dryness in iron vessels, and it should be kept slightly alkaline in order that it may not take up much iron from the pans in which it is being boiled. A small quantity of iron salt in the resulting chloride is not objectionable, however, for it is decomposed at the very outset of the subsequent electrolysis, and the reduced iron does not alloy with lithium. A little sal-ammoniac is now added to neutralise any free alkali, and the mass is fused for electrolysis in an iron vessel, which may, if desired, be the one that shall serve as cathode. The arrangement of the electrolytic plant recommended for use in magnesium or sodium manufacture may be employed. If the former (p. 27) be selected, the rim of the crucible which projects above the flange should be surrounded with a metal tube through which water is circulated, in order to keep it cool and so to produce a thin layer of crystallised salt upon the sides of the

* *Comptes Rendus*, 1893, vol. cxvii., p. 732.

crucible at the upper level of the chloride bath. Globules of lithium, which might otherwise creep up the side, are retained by this layer of solidified salt. The electrolysis must not be continued so long that the lithium forms a metallic connection between the walls of the vessel and the porcelain sheath of the anode carbon, otherwise the same difficulties will occur that were explained in the description of Troost's apparatus. After a sufficient quantity of lithium has accumulated, the method of procedure may be exactly the same as in the extraction of magnesium already described; but there will necessarily be a greater loss of metal in pouring out the contents of the vessel in the case of lithium than in that of magnesium. In order to prevent this loss, the whole charge may be cooled in the melting vessel, but then it is important that the latter should be made conical in shape. The crystallised salt loosens itself in solidifying, and may be easily separated from the walls of the crucible by blows from a hammer applied to the outer surface. The shots of metal adhere firmly to the inner wall of the vessel. They are removed by means of knives or scrapers, and separated from adhering salt by melting them together in a paraffin bath which is kept at a temperature of from 180° to 200° C.; the metal then floats to the surface of the bath, whilst the salts sink to the bottom. From this bath the lithium is removed in perforated ladles; it is afterwards washed in benzene, and then, after re-melting by itself, it is either cast in the shape of small rods, or it is pressed into this form under gasoline (sp. gr. 0·56). It is finally stored in glass tubes hermetically sealed by melting the walls together.

For a permanent installation the sodium apparatus would be used, only in this case it must be remembered that the current density should never be so high as is employed for the extraction of sodium. The deposition of lithium is effected by a current of about 1000 amperes per sq. metre [0·64 amp. per sq. in.] of cathode surface, with an electromotive force of about 5 volts.

The electrolytic method described, as well as the subsequent purification of the metallic product, offers so little difficulty, that the author considers this way of separating lithium from the alkali metals for the purpose of obtaining pure lithium compounds, to be simpler than the troublesome separation of the salts in aqueous solution. The lithium obtained is absolutely free from alkali and alkaline earth metals.

Uses of Lithium.—Lithium has not found application in the arts on account of its high price. The simplicity of the electrolytic extraction process marks it out for use in the production of pure lithium salts. The proposal to use lithium for the generation of hydrogen in aëronautics (1 lb. of lithium affords over 25·5 cub. ft. of hydrogen at 0° C. and at the normal atmospheric pressure) must still be relegated to the future.

CHAPTER III.

BERYLLIUM.

Properties of the Metal.—Beryllium (Be; atomic weight = 9; specific gravity = 1·64) is a lustrous, white, soft, malleable, and tough metal, with a melting point approximating 800° C. In the form of powder, thin sheet, ribbon or wire, the metal burns like magnesium in the air, in the halogens, or in sulphur, &c. Beryllium withstands the action of water better than magnesium, but it is equally readily attacked by acids; in salt solutions it slowly oxidises with evolution of hydrogen.

Occurrence in Nature.—The metal occurs almost exclusively in combination in silicates, of which the principal is beryl, a double silicate of aluminium and beryllium with the formula $(BeO)_3 . Al_2O_3 . 6SiO_2$. The emerald is a form of beryl that is especially prized as a precious stone.

Extraction of the Metal.—Numerous methods are given for the treatment of beryl. The method of fluxing varies but little from that of other silicates, being effected by means of alkaline carbonates. The fusion is afterwards treated with sulphuric acid to render the silica insoluble; and there then results a solution of beryllium, aluminium, and iron salts. The bulk of the aluminium is then separated, either as alum by the addition of potassium sulphate, or as aluminium fluoride, by boiling with cryolite or other fluorides. If the quantity of iron present be neither too small nor too great, it is carefully precipitated by the addition of soda, with the precaution that any ferrous salts shall be previously peroxidised by the addition of alkaline chromate, chloride of lime, or other suitable oxidising agent. On the further addition of barium carbonate, or an alkaline carbonate, a precipitate of aluminium hydroxide will be formed which will carry some beryllium down with it; but the latter may afterwards be separated as beryllium hydroxide by the addition of ammonium carbonate solution to the precipitate. The remaining solution should contain only beryllium sulphate, which must be converted into the chloride or other haloid salt prior to its use for electrolysis. For this purpose the beryllium may either be precipitated as carbonate by means of an alkaline carbonate, the precipitate being then redissolved in hydrochloric acid, or it may be decomposed by means of barium chloride.

The beryllium chloride solution produced by either of these methods is mixed with any chloride of an alkali or alkaline earth metal (excepting that of magnesium or calcium), and is then evaporated to dryness, whereby a mixture of salts is obtained that is very fusible and a good conductor of electricity, and from which the beryllium may be extracted by one of the electrolytic methods that have been described as applicable to magnesium and lithium. A little sal-ammoniac should be added to the solution before evaporation, in order to prevent the formation of too much oxide by the decomposition of the beryllium chloride during that process. Concerning the electrolysis itself there is practically nothing to be said, except that it is conducted in the same manner and in the same class of apparatus as that of magnesium. It should be observed, however, that the melting point of the metal must be only just reached, and as little as possible exceeded, during the progress of the electrolysis, as the beryllium would otherwise alloy with iron. It is of importance, also, that the melting vessels should be made of good weld iron, on account of the somewhat higher temperature required for this process than that of carnallite reduction. Beryllium has not yet found any application in the arts.

SECOND GROUP.

SODIUM AND POTASSIUM.

CHAPTER IV.

SODIUM.

Properties of the Metal.—Sodium (Na; atomic weight = 23; specific gravity = 0·974) is a white metal, the freshly cut surfaces of which exhibit a silvery white lustre; it is soft and may even be kneaded at ordinary temperatures. It melts at 95·6° C., and begins to vaporise at a clear red heat—*i.e.*, at about 900° C. It is capable of alloying with the other alkali metals, and with some of the heavy metals. Of these alloys the amalgam, and the alloys with lead and tin, have found practical use in the arts. Sodium is capable of dissolving in anhydrous liquid ammonia, to which it imparts a blue colour. It oxidises very rapidly in the air, yet it may be melted without danger in a dry vessel over an open flame, provided that it is not heated much above its melting point. Once enkindled in air that is dry and free from carbonic acid, it burns with a yellow flame, and with the evolution of much heat, yielding the peroxide, Na_2O_2. It combines energetically, also, with the non-metals. It decomposes water even at the ordinary temperature, forming sodium hydroxide, and it must, therefore, be stored in liquids, such as petroleum, which contain no oxygen. As a metal which can decompose even water, it is very violently attacked by acids, forming salts which are, almost without exception, easily soluble in water. It is a powerful reducing agent, decomposing compounds of the metals, and even of many non-metals (CO_2, SiO_2, B_2O_3, &c.).

Occurrence in Nature.—In nature it occurs only in the form of salts; as chloride, in rock-salt, NaCl; as fluoride, in cryolite, $Al_2F_6 . 6NaF$; as sulphate, in Glauber's salt, $Na_2SO_4 . 10H_2O$; as nitrate, in Chili saltpetre, $NaNO_3$; as borate, in borax, $Na_2B_4O_7 . 10H_2O$, and other borates; as carbonate, in soda, $Na_2CO_3 . H_2O$, and in trona, $(NaHCO_3)_2 . Na_2CO_3 . 2H_2O$; as silicate, in felspar, &c. For the manufacture of soda compounds on the larger scale the chloride is mainly used; and the metal may be obtained either by a metallurgical reduction process from the carbonate or hydroxide, or by electrolysis from the fused chloride.

1. THE REDUCTION PROCESS.

On the large scale, sodium was first* produced by distilling a mixture of anhydrous carbonate (calcined soda) and carbon; whilst until recently the bulk of the metal was obtained by Castner's method,† which consisted in a reduction of the hydroxide by an intimate mixture of iron and carbon, thus :—

$$3 \, NaOH + Fe \, . \, C_2 = 3 \, Na + Fe + CO + CO_2 + 3H.$$
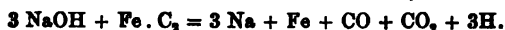
Netto‡ has avoided the use of iron by causing fused caustic soda to drop upon a layer of heated carbon contained in an upright retort or reverberatory furnace.

2. ELECTROLYSIS.

Davy's Experiments.—The electrolytic decomposition of the hydroxides of potassium and sodium led, as is well known, to the discovery of these metals. Davy§ thus described the apparatus which he employed for his research in this direction :—

" By means of a stream of oxygene gas from a gasometer applied to the flame of a spirit lamp, which was thrown on a platina spoon containing potash, this alkali was kept for some minutes in a strong red heat, and in a state of perfect fluidity. The spoon was preserved in communication with the positive of the battery of the power of 100 of 6 inches, highly charged ; and the connection from the negative side was made by a platina wire."

The reasons why this process cannot be used for the production of the alkali metals on a large scale need not be discussed at present; they will become evident from the discussion of later experiments.

A modification of this method has been tried, in which a platinum dish containing mercury and a very concentrated solution of caustic potash is connected to the negative pole of a battery, and the resulting amalgam (formed by the combination of the mercury with the potassium produced by electrolysis) is distilled to separate the alkali metal. But the process is not practically workable, since the expenditure of electrical energy stands in most unfavourable proportion to the yield of metal. The descriptions, however, of both processes contained an item of the highest interest in applied electro-chemistry—namely, *the use of a vessel made of a conducting material, and used simultaneously as the container for the electrolyte and as the pole of the decomposing cell.* This circumstance cannot here be too strongly

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* Brunner, *Schweigger's Journ.*, vol. xxi., p. 201; and St. Claire Deville, *Ann. de Chem. et de Phys.*, 1852, vol. xliii., p. 5.
† United States Patent 342,897, June 1, 1886. [Eng. Pat., 7,395, 1886.]
‡ German Patent 45,105 and 52,555. [Eng. Pat. 17,412, 1887.]
§ *Phil. Trans.* of 1808, pp. 1, 333 ; 1810, p. 16.

emphasised, since modern inventors are constantly endeavouring to pass off this idea as an original discovery.

Watt's Process.—The first suggestion for the manufacture of alkali and alkaline earth metals originated with Charles Watt.* The patent specification ran as follows :—

"The second part of my invention consists of a mode of preparing or obtaining the metals of the alkalies and alkaline earths by the united action of electricity and heat. For performing this part of my invention by the united action of electricity and
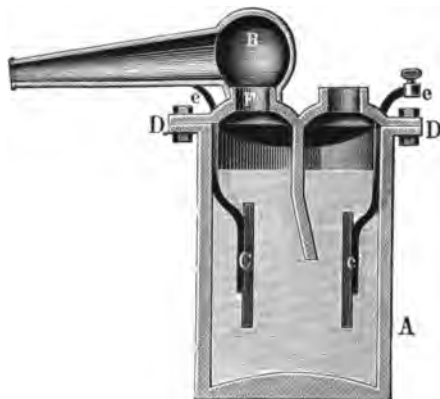
Fig. 19.—Watt's apparatus for the extraction of sodium.

heat I employ a vessel of the form shown in Fig. 19, which is made of iron or other suitable material capable of bearing a full red heat. In this figure, A is the vessel, which should be at least half an inch thick and, if made of iron, previously to its being used should be coated over its exterior with clay or other substance to preserve it from the action of the fire ; B, movable head for the collection of the metals ; C, electrodes, with their attachments, e ; D, flanges to support the vessel upon the furnace. The covered compartment, F, being that in which it is intended to eliminate the metals, is supplied with a carbon electrode, and the uncovered compartment is supplied with a gold electrode ; but I wish it to be understood that I do not restrict myself to the particular form of apparatus, or to the material to be used for electrodes. The vessel is filled with dry saline matter, so that when it is in a state of fusion it shall reach the dotted line [the level shown in the figure] ; the partition keeps the eliminated substances from reacting upon each other, and also excludes the air from the compartment in which the metal is eliminated, the access of which would cause the metal to be oxidised. The vessel is placed in a furnace where it can be subjected

* Eng. Pat. 13,755, Sept. 25, 1851.

to the action of a full red heat, and when the saline matter is in a state of fusion contact is made between the decomposing vessel and the apparatus supplying the electric current or currents, the intensity of which should, at least, be equal to that which would be supplied by ten cells of Daniell's battery arranged for intensity, but, of course, this depends upon the nature of the salt which is being decomposed. The fused salt is maintained at that temperature which will ensure the instantaneous volatilisation of the metal as it is eliminated, and a proper receiver (such a one as is usually employed for the preparation of such metals will answer) is connected air-tight with the narrow tube projecting from the head. The metal is received and preserved in any convenient fluid hydrocarbon. The salts which I usually employ are the chlorides, iodides, or bromides of the metals of the alkalies or alkaline earths."

The salts which the inventor used may have been the haloid compounds of the alkali and alkaline earth metals, as he describes: but neither before nor since the publication of that specification has it been possible to distil in an iron vessel the metals calcium, barium, or strontium, of which the melting points even approximate that of iron. Granted that he merely omitted by accident to explain in his specification that the electrodes were insulated not only from one another, but also from the iron crucible, the inventor must have used a remarkably refractory modification of gold if he succeeded in making from it an electrode which could be employed as the positive pole in a bath of fused alkaline chloride, and thus withstand the action of the nascent chlorine for a sufficiently long time to enable him to accomplish the decomposition of the alkaline halogen salts according to his *usual* methods. The patent was applied for on September 25, 1851, and granted on March 24, 1852.

It is well known that in the summer of 1851, Bunsen succeeded in decomposing fused magnesium chloride into magnesium and chlorine by means of the electric current; and this classical research is described in vol. 2 (p. 137) of Liebig's *Annalen* for 1852. In outward form the apparatus used by Watt shows the closest agreement with that employed by Bunsen, and the difference between them lies in the fact that the latter, which was based on the results of Bunsen's investigation, fulfilled its purpose in every respect, whilst the former was altogether impracticable.

The first success in the electrolytic treatment of the chloride of an alkali metal was obtained by Bunsen and Matthiessen with lithium chloride in the year 1854. This result has already been described (p. 34). Further improvements by Matthiessen, and afterwards by Linnemann, related specially to potassium, and will be referred to under that head.

Jablochkoff's Process.—In spite of Bunsen's discoveries, the decomposition of sodium chloride appears to have involved

considerable difficulties, for until the year 1882 this problem is scarcely referred to in literature. In that year, Jablochkoff[*] devised the apparatus shown in Fig. 20. Here the salt was introduced through the charging funnel D into the clay crucible A, where it was melted and electrolysed. The electrodes *a* and *b* were surrounded with the tubes *c* and c_1 for the removal of chlorine and sodium vapour respectively.
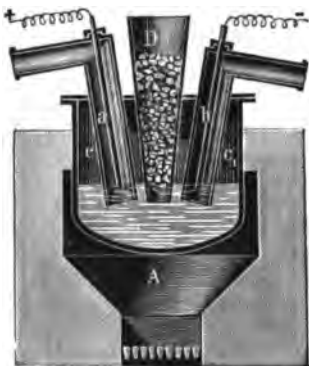
Fig. 20.—Jablochkoff's apparatus for the extraction of sodium.

The practical difficulties which arise in applying such an arrangement to the electrolysis of alkaline chlorides are unquestionably great. They lie chiefly in the designing of a sufficiently durable apparatus. The tube for the removal of the chlorine must not be made of metal; and porcelain, especially in close-grained pieces of the thickness required for the purpose, is very easily broken at the high temperature employed. Then, again, if the tube arranged to convey the metallic vapour to the condenser be made of porcelain or any other material prepared from clay, it will very soon become perforated by the action of the alkali metals in the liquid or vaporous condition. But a metal tube is equally unsuitable. Even if the electrode *b* were insulated from the surrounding tube, the metal sheath would be of little value; because, granted even that it might be possible, by the use of sufficient heat, to maintain so high a temperature that the separation of fluid metal—and therefore the formation of a metallic contact between *b* and c_1—could be avoided, there would necessarily be a deposition of sodium on the outside of the tube throughout the process. This results from the fact that insulated metallic substances placed in the electrolyte tend to form intermediate electrolysing surfaces between the poles, the side of the metal next the anode functioning as a cathode, and that next the cathode acting as an anode. The consequence of this is that intermediate reactions are produced, which cannot but be prejudicial to the working of the process as ·a whole. Under these circumstances the durability of the metallic sheath is naturally of the shortest. Later modifications of the original construction, consisting in the arrangement of the electrodes and of their separating partitions in the form of·concentric tubes, have failed to overcome the difficulty.

Hoepfner's Process.—In the year 1884, C. H. W. Hoepfner [†]

* *Dingler's Polytechnisches Journal*, 1884, vol. ccli., p. 422.
† German Patent 30,414.

patented a process, of which the following is an account derived from his specification :—" Sodium chloride is melted in a crucible, the bottom of which is covered with a layer of copper on silver. Instead of the latter, other heavy metals may be employed, with the exception of mercury, which boils at too low a temperature. The side-walls of the crucible must be made of some non-conducting material. The layer of metal at the bottom of the crucible serves as an anode, and it is, therefore, connected with the corresponding pole of the galvanic battery, or of the dynamo, by means of an iron or copper wire introduced either from below or at one side. If the circuit be now completed by immersing a carbon or metal cathode in the fused chloride from above, a rapid deposition of metallic sodium at once sets in ; the sodium burns in the presence of air, but if the latter be excluded, the metal may be collected or distilled. While the light metal separates at the upper surface, the chlorine attacks the metal of the anode, forming a chloride which fuses at the high temperature of the operation, so that by continuing the current the anode undergoes electrolytic solution; but on account of its weight the chloride remains at the bottom of the crucible."

Hoepfner must have found that by continuing the current the course of the separation did not run so smoothly as was the case at the beginning, for the metallic chlorides do not remain so quietly at the bottom of the vessel as the patent specification suggests. With the density of current required for the deposition of sodium, the copper, silver, or other metal dissolved at the anode would, in a short time, be re-deposited at the cathode in such quantities, and in so slightly coherent a condition, that, in spite of every precaution, it would be washed off again by the fused salt, and (especially in this form of apparatus) would be returned to the anode. Not only would there be no chlorine evolution, which the invention aims at avoiding, but in a short time there would be no deposition of alkali metal either.

Rogers' Process.—A. J. Rogers[*] has patented the apparatus shown in Fig. 21, which is a longitudinal sectional elevation of the whole apparatus along the line $y\,y$ (Fig. 22), and in Fig. 22, which is a plan of one portion of the apparatus along the line $x\,x$ (Fig. 21). A' shows the masonry, B the fire-grate. The melting-pot, C, is provided with a cover, C', which may be fastened down; on the middle of this cover is a funnel, c', which closes automatically by a ball-float valve, c, when the crucible is sufficiently charged. The safety-valve, c_2, is provided to guard against risk from a sudden evolution of gas. The decomposing-vessel, D, is divided into two compartments by the wall, d, which is made of some porous material, such as fire-brick, and reaches nearly to the bottom of the chamber.

The tube, E, forms a connection between C and D, and a cock,

[*] United States Patent 296,357, April 8, 1884.

e, serves to regulate the flow of melted material from C to D. N is the negative, and P the positive electrode; the wire connections for the electrodes within the cells are insulated, and at the same time protected from the attack of acid, gases, &c., by the fire-clay tubes *n* and *p*, in which they are respectively enclosed. The tightly-fitting cover, *d'*, is connected by two necks, F F', with separate condensers, and is fitted with four closed doors at the points *f f* and *f' f'* shown in Fig. 22. The
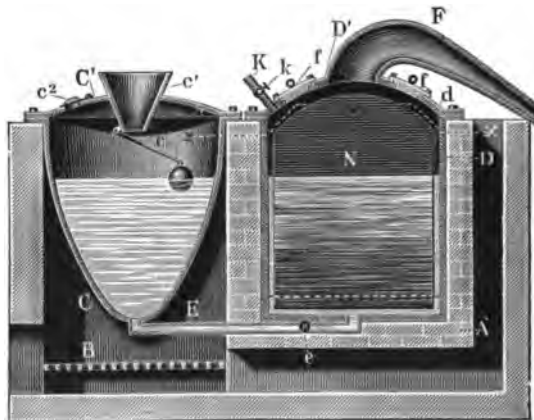
Fig. 21.
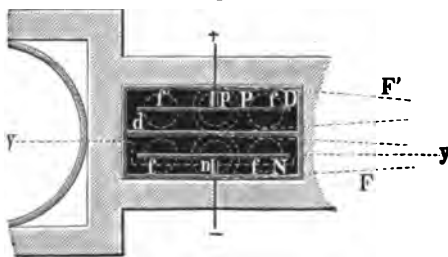
Fig. 22.
Rogers' apparatus for the extraction of sodium.

separating partition, *d*, must be gas-tight even up to the top of the roof D'. Through the roof of the negative compartment is passed the pipe, K, with the valve, *k*, by which hydrogen or other reducing gas may be introduced. The vessel, D, is set in thin masonry, and must be constructed of a non-conducting and fire-resisting material, and should be about 1 ft. wide, 3 ft. long, and 4 ft. deep. The decomposing vessel bears a strong resemblance to that of Watt's, but it is not so faulty in the details of its construction. Nevertheless, it is scarcely to be expected that it could be advantageously used for the reduction of the alkali

metals ; and the material of which it is made is incompatible with
great durability. The distillation of sodium in clay vessels is an
undertaking of very doubtful expediency. The iron pre-heating
vessel, C, filled at a strong red heat with melted salt, would,
by its own weight, become unserviceable after a few hours. To
attach the tube, E, sufficiently firmly to the clay vessel, D, and
to maintain a tight joint when the whole apparatus is charged
with fused sodium chloride at a red heat, would be no easy task.
Rogers has, meanwhile, had an opportunity to discover the
faults of the apparatus.

  Omholt's Apparatus.—Omholt's plant[*] (Figs. 23-26) for the
continuous production of the light metals, appears also to belong
to that class of inventions which are first patented and then, when
opportunity offers, are put to the practical test. The patentee
writes :—"The apparatus shown in longitudinal section (both in
elevation and in plan), in Figs. 23 and 24, consists of a
reverberatory furnace, with the hearth divided into two separate
compartments by the bridges, *a a*. In each of these compart-
ments are two half retorts, *b* and *c*, borne horizontally and
parallel to one another, on supports, *d d*, of fire-resisting
material, placed side by side, in such a way that the half retorts
are separated by a short space from the sole of the hearth. The
half retorts marked *b b* contain the negative electrodes, *e e*,
whilst those marked *c c* enclose the positive electrodes, *f f.* The
halogen compound to be electrolysed lies melted on the hearth
at such a height that the electrodes in the half retorts are com-
pletely immersed. The metal separating at the cathode, and the
halogen set free at the anode, collect within their respective half
retorts, and are there protected from contact with the furnace-
gases, owing to the liquid seal which is formed by the dipping
of the half retorts into the melted charge. The half retorts are
made of a fire-resisting and non-conducting substance, and are
coated on the interior with a lining of carbonaceous material.
The latter material consists for the most part of carbon (graphite
or wood-charcoal) ; the mixture used, for example, in the manu-
facture of plumbago crucibles being suitable. The admixed clay
serves only to give plasticity to the carbon.

  "The electrodes are made of carbon or other resisting material.
They lie lengthwise within the half retorts, as shown in the
illustration, whilst at the one side (at *g* in Fig. 25) they penetrate
the masonry of the furnace, and there make the necessary con-
nections for the circulation of the electric current. To prevent
the separation of halogen or metal on the electrodes outside the
half retorts, the exposed portions between the face of the retorts
and the brickwork of the furnace are insulated by a covering
of fire-clay. By this construction, I [the patentee] allow for the

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[*] German Patent 34,727, June 6, 1885.

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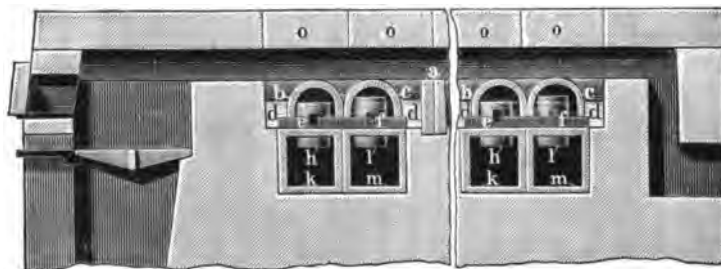
Fig. 23.—Omholt's Sodium Plant (longitudinal sectional elevation).
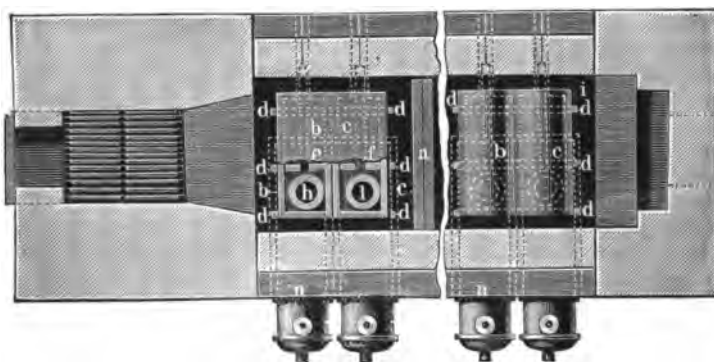
Fig. 24.—Omholt's Sodium Plant (plan).
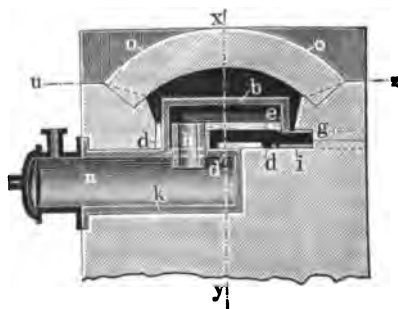
Fig. 25.—Omholt's Sodium Plant (cross section).

renewal of broken half retorts without damaging the electrodes or altering their position.

"The half retorts, *b b*, are connected with the fire-resisting fore-

chambers, $k\,k$, by short tubes, $h\,h$, which should be as wide as possible and which are best placed vertically; these tubes, $h\,h$, are made of some mixture containing carbon. The position of the upper edges of the tubes, $h\,h$, determines the level of the melted charge in each compartment of the hearth. The metal separating at the electrodes, $e\,e$, collects under the half retorts, $b\,b$, on the upper surface of the fused salt, whence it passes, either as liquid or as vapour, through the tubes, $h\,h$, into the fore-chambers, $k\,k$, beneath, where it accumulates in vessels placed to receive it. Each fore-chamber, k, is closed by a mouthpiece, n, similar to those used in connection with coal-gas retorts, through which the vessel placed beneath the pipe, h, may be withdrawn when it is fully charged with metal, and replaced by an empty one. These vessels are removed as quickly as possible from the fore-
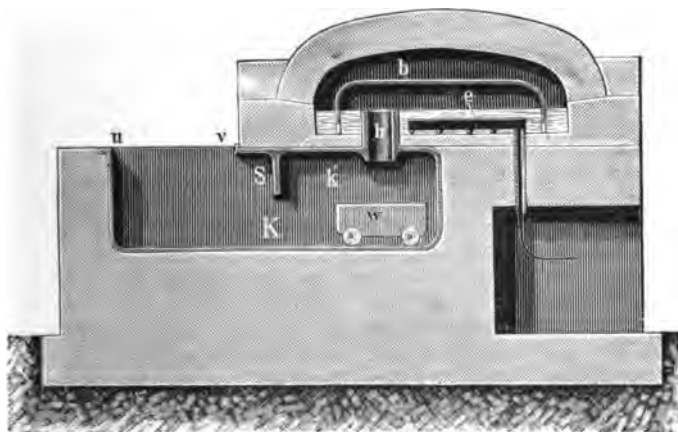
Fig. 26.—Omholt's modified Sodium Plant.

chambers, and are allowed to cool either in a neutral gas or in such a way that air is excluded. A neutral gas is also passed into the fore-chambers, $k\,k$, to the complete exclusion of air.

"The halogens produced in the half retorts, $c\,c$, are led away after the manner of removing the metallic vapours just described, but the upper margins of the upright tubes, $l\,l$, project slightly above the level of the fused salt in the furnace, in order to guard against an overflow of the liquid into the fore-chambers, $m\,m$. The halogen is conveyed from the latter by means of a pipe connection. The halogen compound may be charged into the hearths continuously or intermittently, and either in the solid or in the fused condition. To prevent the contamination of the melt by ashes from the fuel or the like, the furnace may be constructed like a muffle or muffle-furnace. The use of gas-firing is also to

be recommended: To facilitate the exchange of worn-out or broken half retorts, the furnace arch may be constructed with removable fire-clay blocks, *o o*. Instead of arranging the electrical connections of the electrodes at the side, as in Fig. 25, it is more practicable to make them from below, as in Fig. 26, where the electrode, *e*, is supposed to be the cathode; the anodes, however, are similarly connected up with the dynamo from below.

"To avoid the use of neutral gases, I [the patentee] effect the removal of the light metal accumulating on the surface of the melted charge in the half retort, *b*, in such a way that it passes through the upright tube, *h* (Fig. 26), into a fore-chamber, *k*, which is so far filled with inactive liquid (*e.g.*, a petroleum product of high boiling point) that the curtain wall, S, of the compartment, *k*, forms a liquid seal, preventing the access of the outside atmosphere. The light metal flowing through *h* collects in a movable vessel, *w*, placed beneath, which may be drawn out when full, raised through the entrance, *u v*, of the fore-chamber, K, and replaced by another empty vessel."

So far the patent specification. No one who has had any experience in the electrolytic separation of the metals of the alkalies, earths, or alkaline earths in vessels, which are placed in direct contact with the furnace-gases, and which are made of such porous material as are the half retorts described by Omholt, will have a moment's hesitation as to the verdict upon this process. The furnace-gases have, especially in the reverberatory furnace just described, the most favourable opportunity to circulate in intimate contact with the fused chloride, whilst they are separated from the vapour of sodium only by a partition that is especially pervious to gases. The rate at which the metal is separated is reduced in proportion as the resistance of the electrolyte increases; the rate at which the bath of chloride becomes loaded with oxides and hydroxides being proportionately very great. This latter circumstance is a result of the contact of the hot furnace-gases with the charge, either directly or after diffusion through the partition wall, and is in part due to the oxidation of the metal and in part to the decomposition of the chloride.

The small yield of metal, and the increasing resistance of the bath, in consequence of the absorption of oxygen, would alone suffice, for practical purposes, to condemn an apparatus of this description. It should be noted also that the electric resistance of the bath would continue to increase with the lapse of time, owing to the extraction of alumina and silica from the masonry, until finally the current would cease to pass. In passing unfavourable judgment upon this plant, no account has been taken of the losses resulting from the greater irregularities that must occur, such as fracture of retorts and other evils. Moreover, the use of an oil reservoir (Fig. 26) under the thin hearth of a

reverberatory furnace, filled with a fused mass at a red heat, and especially liable to wear out, would scarcely be permitted in countries in which the works are subject to Government inspection, even of the most lenient description.

Fischer's Process.—F. Fischer [*] has described his experiments with the arrangement shown in Fig. 27, as follows:— "An iron crucible is divided into three compartments by two transverse partitions, reaching nearly to the bottom. The dry alkaline chloride is introduced into the first division in such quantity that the level of the melted salt in the closed decomposition compartment may stand at about that of the line *a*. The carbon plate, *c*, which serves as anode, is either continued upwards through the cover of the cell, or makes connection with the electric generator by a protected metal wire. An iron plate, *e*, may serve as cathode, and the sodium vapour produced is carried off by a side tube. The metal walls of the anode compartment must be protected from the action

Fig. 27.—Fischer's apparatus.

of the chlorine as it is evolved and conducted away; but this difficulty would disappear if the carbonate were used for the decomposition." The electrolytic dissociation of the carbonate, however, offers very great difficulties, in consequence of the small electrical conductivity of this salt. The use of the chloride leads to the same troubles that are experienced with Troost's apparatus (p. 34).
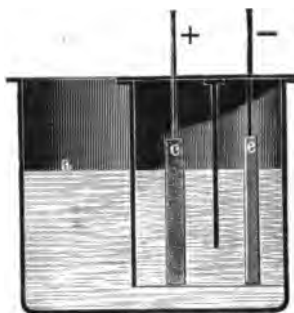
Hornung and Kasemeyer's Plant.—The apparatus of Hornung and Kasemeyer [†] is distinctly retrogressive. This arrangement is shown in Figs. 28 and 29: "In which A is a graphite anode, serving also as a crucible for melting the charge, and enclosed within an iron sheath. Attached by the usual devices to the rim of the crucible is the ring-shaped cover, P, made of a close-grained porcelain, and provided with a channel, leading to an off-take main, C. Within this cover is hung a [tube-shaped] porcelain screen which is long enough to be immersed to a sufficient depth in the electrolytic bath. Through this screen the hollow cathode, K, made of iron or other suitable metal, is lowered into the space within the anode. The cathode must be of such width that a space is left between it and the tube, S. At the upper end of the cathode a compartment, *e*, is formed, of which the under side

[*] Wagner-Fischer's *Jahresbericht*, 1886, p. 222.
[†] German Patent 46,334, Jan. 29, 1888.

makes a tight joint with the cover, P, and the shell, S.   This chamber is closed above, but is provided with a number of perforations, k, below, through which free communication is made with the space between the cathode and the tube, S.   At the side of the chamber is a tube, M.

The cathode is open at both ends; and through the upper opening, the original charge is introduced, with the aid of any of the usual mechanical devices for such a purpose, and afterwards chloride is added, to make good that which has been decomposed during the electrolysis; this is done in such a manner that the cathode may always remain perfectly full of salt, which thus forms a close cover to the apparatus at this place.   The lengths of the cathode and of the anode, respectively, are so chosen that the weight of the chloride charge in the former may suffice to maintain the level of the liquid in the anode-cell at such a height that all communication is cut off between the two compartments formed by the screen-tube, S. The chlorine formed at the anode and the sodium vapour produced at the cathode, during the progress of the operation, are kept apart by
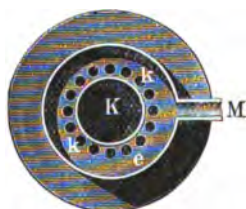
Fig. 28.   Fig. 29.

Hornung and Kasemeyer's apparatus.

the screen, S, the former passing to the tube, C, the latter to M. In proportion to the decomposition of the salt, fresh chloride sinks into the bath from the cathode, and this is continuously replaced by fresh additions above."

The whole arrangement strikes one as being a most unfortunate combination of devices of which each separately has been thoroughly serviceable amid its original surroundings. For example, the use of a carbon crucible as a combined decomposition vessel and anode has proved successful in the apparatus which Bunsen * employed in 1854 for the reduction of chromium

* *Pogg. Ann.*, 1854, vol. xci., p. 619.

(see *Chromium*). The employment of hollow electrodes through which the solid electrolyte might be charged, dates back even farther, for J. H. Johnson's application for provisional protection in England, described such an arrangement in 1853 (see *Aluminium*). The inventors have now discovered that the sinking of the substance in the tube does not take place uninterruptedly, and have introduced a rotating spiral within the electrode in order to prevent stoppage. The separation of the electrodes, and of the ions produced upon them, by means of non-conducting partition walls, is as principle a old as electro-chemical decomposition itself.

If the metal and halogen are to be separated in Hornung and Kasemeyer's apparatus, it is necessary to replace the short separating tube by a cell closed at the bottom and provided with perforations at the sides. But even then the life of the iron crucible cover could not be very long, since the metal is surrounded with the heated furnace gases without, whilst within it is in contact with chlorine which has diffused through the substance of the graphite crucible. Among the apparatus previously described there are some which, although they have a few faults, yet possess the advantage of comparative simplicity.

Grabau's Apparatus. — Although the ideas embodied in some of these inventions are undoubtedly good, it is not possible that the processes could be employed satisfactorily for continuous work, nor could they compete with the chemical methods employed for the reduction of the alkali metals from their hydroxides or carbonates. That the source of the difficulty lies in the technical application of the process is shown by the account published by A. J. Rogers,[*] who was able to produce 2·5 to 3 kilogrammes [5·5 to 6·5 lbs.] of sodium from the chloride *per electrical horse-power* in 24 hours, *provided that the apparatus was sufficiently durable* to allow of uninterrupted work. The electro-chemical efficiency of the process was therefore very high, but the apparatus employed was still imperfect. In the same year that Rogers' paper was published, Grabau patented his apparatus which was intended primarily for the electrolytic extraction of alkali metals from their halogen compounds; the patent specification [†] was published on May 2, 1890. In this arrangement the melting vessel, A (Fig. 30), was surrounded by an air-bath, L, heated by the hot gases, which circulated in the space, G, around it. Within this vessel were a bell-shaped cathode-cell, B, made of porcelain or other suitable fire-resisting material, and the carbon positive electrodes, C, which were arranged around the latter. The whole was closed by a cover, D.

At the bottom of the cell, B, the side walls, *w*, are first

[*] *Journal of the Franklin Inst.*, 1889, vol. cxxviii., p. 486.
[†] German Patent 51,898, October 8, 1889. [English Patent 15,792, October 8, 1889].

extended outwards, and are then curved upwards again, so that they ultimately project above the level, N N, of the fused electrolyte. In this way a space is provided between the wall of the cell, p, and the outer jacket, w; and as melted matter cannot penetrate this space, the fused salt does not come into contact with the outer surface of the wall, p, and it is thus impossible that the cell-walls can permit any direct electrical connection to be made between the melted matter within and that without the cathode cell.
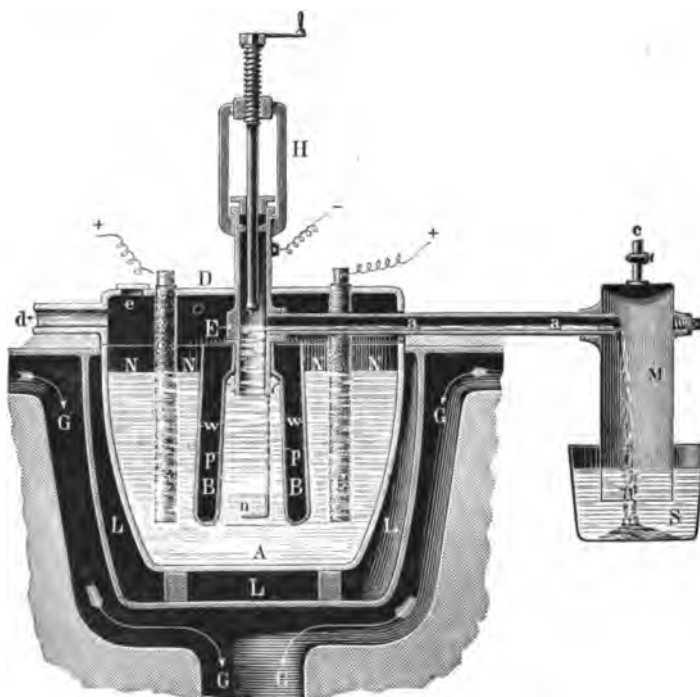
Fig. 30.—Grabau's apparatus for the reduction of alkali metals.

The electrode cell, B, is connected by a tight joint, with a hollow iron cap, E, from which a side tube, a, passing over the rim of the melting vessel, makes communication with the receiver, S. The cap, E, forms the negative pole, and makes electrical contact with the fused salt by means of the rod, n, placed within the bell. The screw-plunger attached to the frame, H, is provided for the purpose of removing any stoppages that may occur in the tube, E. Since the alkali metals are specifically lighter than their chlorides in the fused state, the fluid metal accumulating

in the cathode cell is forced upwards by the pressure of the melted electrolyte, and flows off through the tube, *a*, as fast as it is produced. It is collected outside the decomposition cell, as, for example, in a vessel, S, containing petroleum. In this instance the cylinder, M, may be filled with a neutral gas admitted through the tube, *c*. The chlorine evolved at the anodes during electrolysis escapes through *d*, whilst the charge of salt is introduced into the melting vessel through *e*.

In a supplementary patent dated September 19, 1890, Grabau * recommends the use of a mixture of three chlorides (of sodium, of potassium, and of an alkaline earth) in equivalent molecular proportions, the advantages thus gained being:—a greater fusibility of the mixture, the prolongation of the life of the vessel, and an improved yield of metal. The resulting sodium is said to be nearly free from potassium and alkaline earth metal.

Grabau's process would have solved the problem of the production of sodium by the electrolysis of the chloride, if the difficulty of designing a durable plant of sufficient size on this model could have been overcome. It is not improbable that such an apparatus, if once set in operation, might last for a day or even for a week; but the starting of the process would necessitate many breakages, and every derangement of the plant that calls for a suspension of the process might entail the loss of the whole apparatus. The mixing of several salts to effect a reduction of the melting point is not new, for Bunsen and Matthiessen have frequently referred to the principle ; and the same may be said of the observation that, under certain circumstances, the alkali metal is alone separated in the electrolysis of mixtures of alkali and alkaline earth chlorides.

In the author's experiments, which he undertook rather with the object of obtaining alkali metals than with that of producing pure sodium, he started with the very fusible mixture of $KCl + NaCl$; but he has demonstrated that even in this case, if the current density be not excessive, and if fresh sodium chloride be introduced as fast as this salt is decomposed, the metallic sodium obtained by electrolysis will contain only a small proportion of potassium.

Borchers' Apparatus.—The apparatus used is shown in Fig. 31. The melting vessel, G, had an opening surrounded by the socket tube, M, and two other openings with tubular necks, R. The double-socket porcelain tube, J, fitted into the socket, M, and in this again fitted the iron socket tube, N. N was closed

* [English Patent 16,060, October 9, 1890. In this specification Grabau proposes to employ equi-molecular proportions of potassium and sodium chlorides, and to add 2 molecules of strontium chloride for every 6 molecules of the mixed alkaline chlorides. Strontium chloride was preferred to the calcium salt, because it is more easily obtained in the anhydrous state ; but either (or barium chloride) may be used. The sodium produced contains no strontium, but may retain 3 per cent. of potassium.—TRANS.]

above by an iron plug, through which was passed the iron rod, K ; the latter served as cathode, and was therefore partly immersed in the fused salt. The sodium separating upon the lower part of the cathode floated upwards through the tube, N, and collected there until it overflowed through the side tube, *n*, into a suitable vessel placed to receive it. The level of the melt was, of course, maintained sufficiently high to enable the overflow of the sodium to take place ; and the liquid was prevented from forcing its way through the flanges by means of metallic lead.

Within the neck, R, the porcelain tube, C, was suspended,
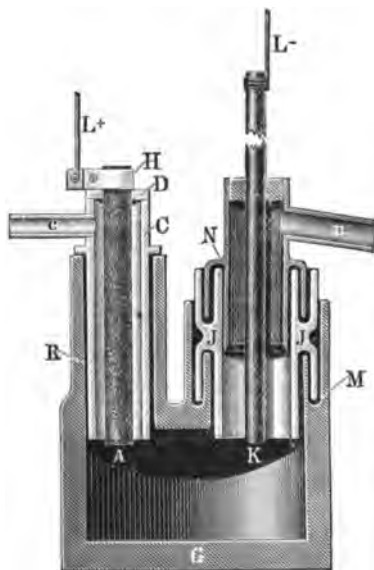
Fig. 31.—Borchers' apparatus for reducing the alkali metals.

and within this again was the carbon anode-rod, A, which was held by the copper grip, H, resting upon the annular cover, D. The chlorine was conducted away through the tube, *c*. A third tube (not shown in Fig. 31) of the same height and width as R, served for the introduction of the electrolyte. The apparatus was designed for use with a current of 30 to 50 amperes, and afforded a yield of from 65 to 70 per cent. of the weight of metal theoretically possible.

This apparatus has not proved to be very durable. Cast iron, at a red heat, will not for long withstand the effects of alkaline chlorides on the one side and of furnace gases on the other. Of the porcelain components, the double-flanged tube

was found to be very readily broken, a fault which would become more serious as the size of the plant was increased.

Requirements for an Electrolytic Sodium-Extraction Apparatus.—Both this apparatus and that devised by Grabau possess the disadvantage that sodium is brought into direct contact with porcelain, for there must inevitably be a loss of sodium caused by the action of the metal upon aluminium silicates at these points, whilst the porcelain itself is rapidly corroded. The lessons that may be derived from the negative results hitherto obtained may be summed up shortly in the following rules for the construction of a suitable apparatus for sodium extraction:—

1. A refractory metal only may be used as the material for the cathode—preferably the better sorts of iron.

2. The alkali metal must be collected in, and conveyed from, the cathode cell without coming into contact with any reducible substance.

3. The walls of the cathode chamber may be made to serve also as cathodes, but in that case they must not be in contact with the electrolyte on their outer surfaces.

4. The anodes must be made of carbon.

5. The anode-compartment must allow of an easy escape for the halogen; and its walls must be made of some material that will withstand the action of the halogens and haloid salts.

6. The walls of the anode compartment must not be in contact with the separated metal.

7. No metallic object must be immersed in the electrolyte in any position between the poles or in the path of the current.

8. The whole apparatus must be made of a fire-resisting material.

These conditions are only at present fulfilled in two forms of apparatus, of which the former is that introduced by Grabau in 1891, as an improvement on his earlier invention. It differs from it only in the arrangements of the cathode bell, so that this alone now requires explanation.

Grabau's later Apparatus.—The modern Grabau cathode-
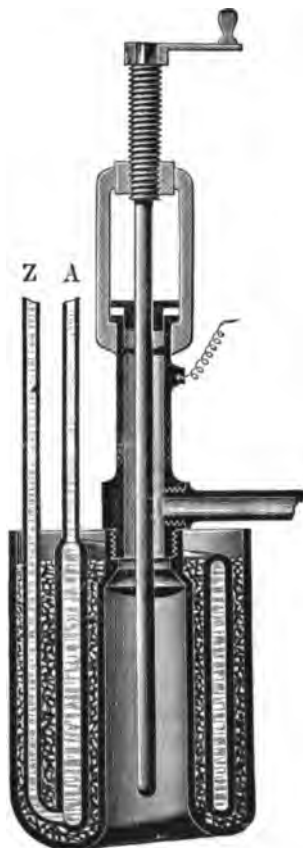
Fig. 32.—Grabau's modified cathode cell.

cell has a wider space than that originally provided between the bell and its bent outer wall. In this space is arranged a cooling tube with connecting pipes, Z and A, for the admission and removal respectively of a cooling liquid. The object of this is to maintain a thin crust of solidified salt upon the outer wall of the cell; and in order that the crust may not become too thick the cooling tubes within the U-shaped jacket of the bell are packed in a material having a low conductance for heat. The temperature of the fused salt within the bell is maintained sufficiently high to prevent solidification on the inner walls, owing to the enormous density of the current that is here passing through the electrolyte.

Borchers' Sodium-Extraction Plant.—Another form of

Cooling Water: Escape.—Cooling Water: Admission.

Figs. 33 and 34.—Borchers' sodium-extraction plant.

apparatus has been constructed by the author for use in two works, and was described by him* in 1893. This apparatus is

* Borchers "Alkalimetalle", in the *Zeitschrift für angewandte Chemie,* 1893.

shown in Figs. 33 and 34, which are about one-eighth of the full size. It consists of two chambers connected together by a special joint. One of these, the cathode chamber, K, is of iron, whilst the other, the anode compartment, A, is of chamotte. Thus the anode, *a*, is provided with a shield through which no chlorine can pass to the cathode, and which cannot be attacked from without by the fused salt, or from within by the powerfully-reducing metal obtained at the cathode. It is in this way possible to use tube-shaped cathodes for the collection and removal of the metal, the advantage of which is that the deposit can be produced only upon the inner side, for the outer surface is nowhere in contact with the electrolyte.

Great difficulties were encountered at first in making a good joint between the vessels. It was accomplished, as shown in Figs. 33 and 34, by means of a hollow metal water-cooled ring, R, held together above and below by the clamps, Z. The only really impermeable material that is available for such portions of an apparatus is the electrolyte itself solidified by cooling, no other material being able to withstand for long the action of the fluid salts. The breakage of the fireclay portion of the apparatus is avoided by placing an asbestos-washer between the water-cooled ring and the flange of the anode-compartment, A, in order to minimise the difference of temperature between the adjacent parts. A tube, C, is provided to carry off the chlorine. A sieve, S, with a little asbestos resting upon it is provided to receive the small crystals of added salt, which would otherwise be apt to crack the anode-vessel.

The current density on the cathode, K, must amount to about 5000 amperes per sq. metre [3·2 amp. per sq. in.]. A smaller current density at the anode surface would necessarily lead to an economy of power, but it is scarcely to be attained in an apparatus of the kind employed for the electrolysis of fused lithium and magnesium salts. In this respect the new arrangement offers distinct advantages, for, with the same current density at the cathode, that at the anode may be reduced to any required degree, and the expenditure of power must then show a corresponding diminution.

Castner's Process.—Before passing to the details of the manufacture, mention may be made of several forms of apparatus which have been before the public for about the same time as those just described, but which, with one exception, must be reckoned unserviceable. This exception is the plant devised by Castner.* Whether the system proposed by this inventor is the best remains to be proved. It is to be observed that he recommends the electrolytic decomposition of an alkaline hydroxide. Not only is this a very costly raw material, but it affords hydrogen along with the metal under the action of the

* German Patent 58,121 ; and English Patent 13,356, 1890.

current; and it cannot always be ensured that the value of the energy expended in liberating the hydrogen shall be recovered by the utilisation of that gas.

The apparatus (Fig. 35) consists of an iron melting-pot, A, into which the cathode, H, is inserted through the bottom. To hold the cathode in position and to ensure a good joint, the lower and somewhat narrowed part of the vessel, with the tube, B, which is attached to it, are both filled with caustic alkali before starting the electrolysis, and this in a short time solidifies. The bath of caustic alkali, E, is kept in the fused condition by a gas flame, G; and in this bath are immersed the anodes, F, which (for this electrolyte) may be made of metal. They are suspended from the cover, and are separated from the cathode by a cylindrical diaphragm of wire mesh, M. Above M is
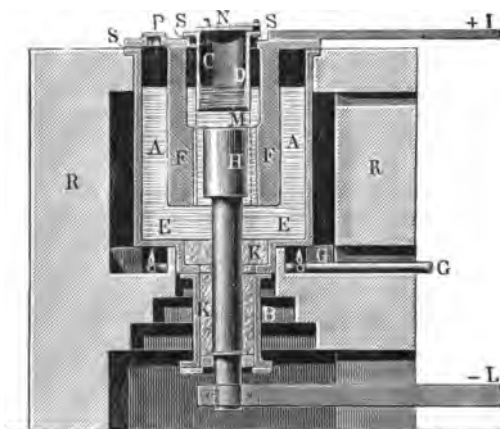
Fig. 35.—Castner's electrolytic sodium-extraction plant.

placed the collecting tube, C, by which the metal (D) and hydrogen are kept separated from the liberated oxygen, which finds an escape from the anode compartment by the opening, P, in the cover. The tube, C, is closed by a lid, N, that rests sufficiently loosely upon its support to permit the escape of hydrogen. For the removal of the liquid sodium, Castner uses a perforated ladle which is able to retain the metal by reason of the high surface-tension of the latter, while the caustic soda drains away through the perforations. The various parts of the apparatus are separated by asbestos card as shown at S. I and L are the dynamo leads. Large quantities of sodium are now being made by this plant.*

* [The Castner process is now in extensive use, not only at the inventor's works in Oldbury, but also at those of the Niagara Electro-Chemical Company in the United States, and of Messrs. Meister, Lucius, and Brunning in Germany.—TRANSLATOR.]

An invention patented by Niewerth* of the firm of Hasen-clever & Sons, and consisting in the decomposition of vaporised compounds of the alkali or alkaline earths by means of frictional electricity, or by induced electric currents, is scarcely to be taken seriously. So also Bull † and Störk ‡ have proposed the introduction of impracticable arrangements into the construction of their apparatus.

Manufacture of Sodium by Electrolysis.—The explanations given on the preceding pages suffice to show that the decomposition of fused sodium salts is surrounded with far greater practical difficulties than is that of the corresponding lithium and magnesium compounds. The causes of this difference are obviously to be explained only after observing the properties of the raw material used for electrolysis and of the products of the operation, or possibly those of some intermediate products. Hence comparisons of the melting points, both of the electrolytes and of the metals to be separated, and of the boiling points of the latter, will throw some light on the question.

Reduction of	Electrolyte.	Melting point		Boiling point of the metal.
		of the Electrolyte.	of the metal.	
Magnesium.	Carnallite.	Degrees C. 500	Degrees C. 500 to 600	Degrees C. over 1100
Lithium.	Lithium-Potassium chloride.	500	180	1000
Sodium.	Sodium-chloride.	900	96	900

From this table it will be seen that in the first two cases the melting points of the electrolytes of the metals agree more closely with one another than do the fusing points of the electrolytes with the boiling points of the metals. But in the last instance, the very low melting temperature of the sodium is far below those of the electrolytes most highly recommended; whilst the boiling point of the metal is practically identical with the melting point of the electrolyte. It has often been supposed that sodium is capable of uniting with sodium chloride to form a sub-chloride, and that the production of this chloride is a function of the temperature. Although this surmise is not absolutely proved to be correct, it appears probable, because it always happens that the higher is the temperature of the electrode, the more unfavourable is the yield of sodium. If a sub-chloride were formed, it should for the most part be re-converted into chloride at the anode; and this reaction would account for the consumption of a correspondingly large proportion of the current.

* German Patent 65,921. † English Patent 10,735, 1892.
‡ German Patent 68,335.

The foremost requirement, therefore, for the successful reduction of sodium by electrolysis is an electrolyte melting at the lowest possible temperature. It is a well-ascertained fact that a mixture of salts fuses at a temperature which is usually lower than the melting points of the individual salts forming the mixture. This fact was utilised even by Bunsen and Matthiessen to guide them in the choice of an electrolyte with low fusing point. At a later date, a mixture especially suitable for the extraction of sodium, and corresponding to the formula $NaCl . KCl . SrCl_2$, was patented by Grabau.* [See footnote on p. 57]. Pure sodium cannot, however, be obtained when such a mixture is employed, for the metal must always contain at least a small proportion of potassium. For most of the practical applications of sodium the presence of a little potassium in the metal is of no consequence; but if the sodium is to be used for reductions in aqueous solutions, it must not be forgotten that the addition of only a few per cent. of potassium will cause the action of the metal upon water to be unduly violent. For such purposes, therefore, a purer metal is required; and this may be produced from a readily fusible mixture of sodium chloride, with haloid salts of strontium, barium, or calcium. But the use of calcium chloride is to be avoided, because this salt gives rise to the formation of basic salts and to the precipitation of feebly conducting deposits on the electrodes. A current density of 5000 amperes per sq. metre [3·2 amp. per sq. in.] should be arranged for, and this, under the conditions of the experiment, will require an average electromotive force of about 10 volts.

For the manufacture of sodium in bulk, it is an unfortunate circumstance that the plant at present available can only be of very limited size. The author has no information as to the maximum dimensions hitherto attained with the Grabau apparatus, but states that the size of his own plant has not yet exceeded twenty times that of the actual illustration given (Fig. 36). This size of plant has been adopted in an installation, still awaiting completion, for the production of 4 cwt. of sodium per day of 24 hours.

It may be well to offer some suggestions as to the management of an installation of this nature. The electrolytic apparatus is set in a heating chamber in the manner shown in Fig. 36; and the use of a separate combustion chamber is just as much to be preferred to that of direct firing as in the reduction of magnesium referred to in a previous chapter. It is true that the expenditure of fuel is greater in this case than when direct firing is resorted to; but as very little external heat is required during electrolysis, owing to the high intensity of the electric current employed, and as in direct firing a considerable loss of fuel may result from an accident to the melting vessel, the arrange-

* German Patent 56,230; [English Patent 16,060, 1890.]

Scrubber

Gas-Producers.

Boiler.
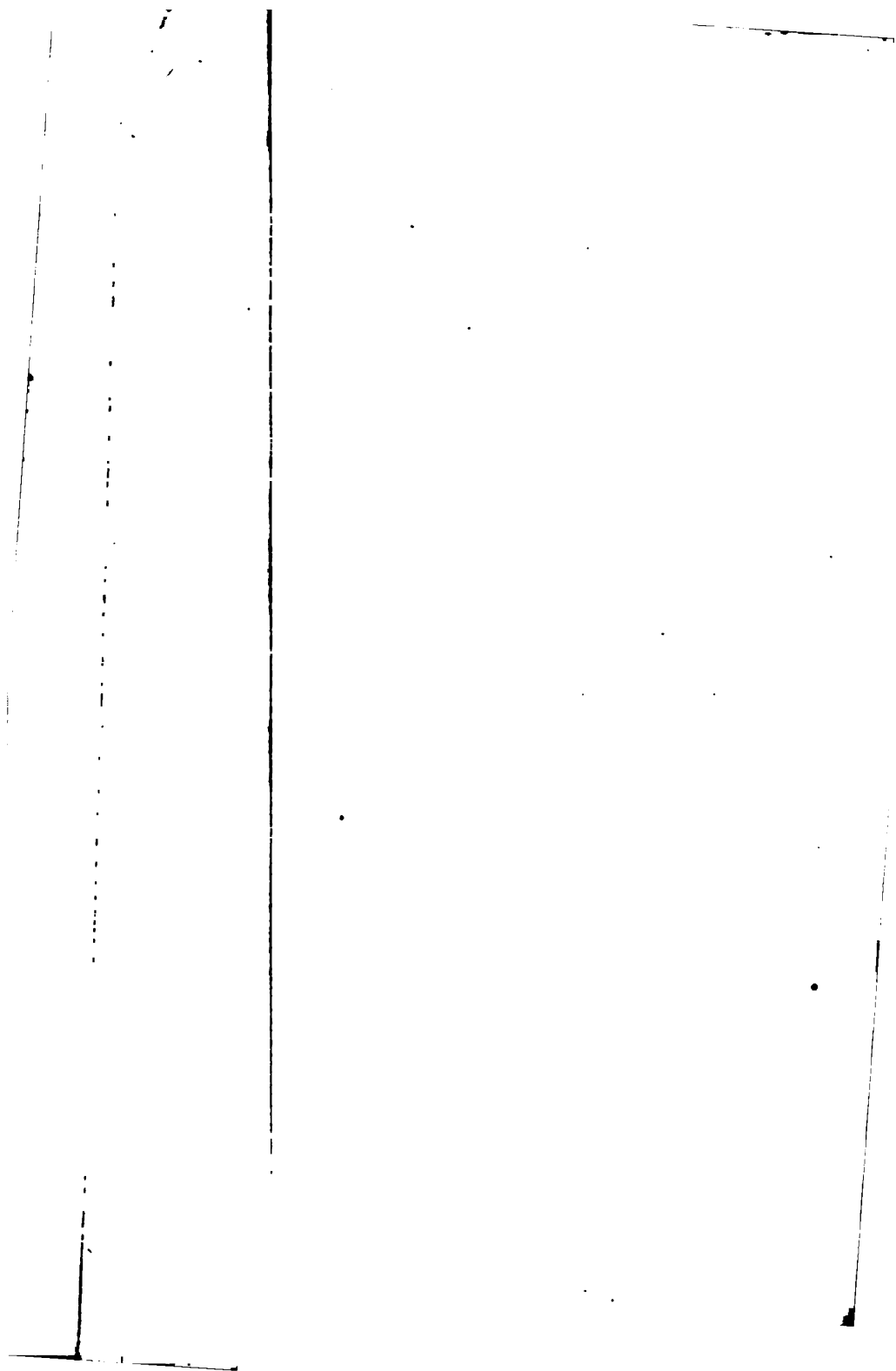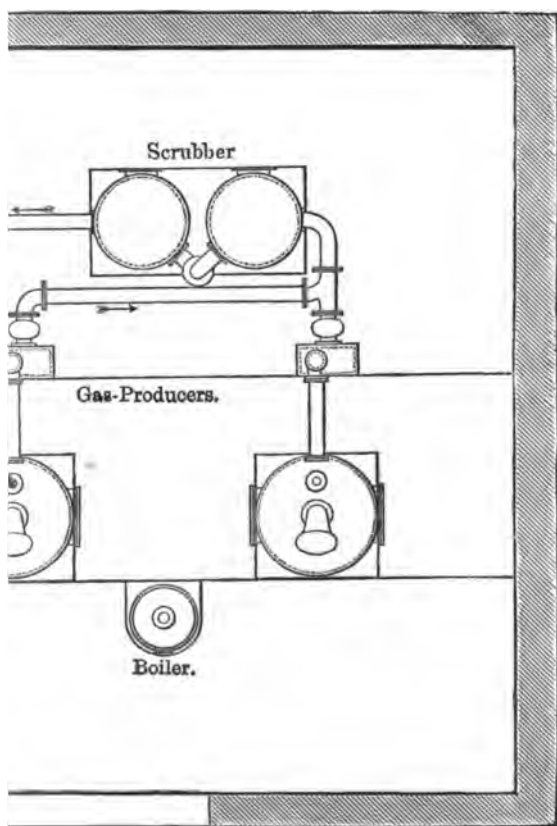
ment recommended is considered to be admissible. A burner for powdered, liquid, or gaseous fuel may of course be substituted for the grate indicated in the drawing. It is not advisable to expose the decomposition vessel freely to the furnace gases, because in the first place, the anode vessel is made of porcelain or of good chamotte, and must therefore be carefully protected from sudden changes of temperature. But in addition to this, the action of the furnace gases on the outside, and that of the fused salt on the inside, of the apparatus, must not be lost sight of; for even the most close-grained clay vessel cannot be considered as absolutely impermeable, and the formation of readily fusible sodium silicate, from the reaction of the silica of the porcelain or clay with sodium chloride absorbed from within, and with oxygen taken from the flame
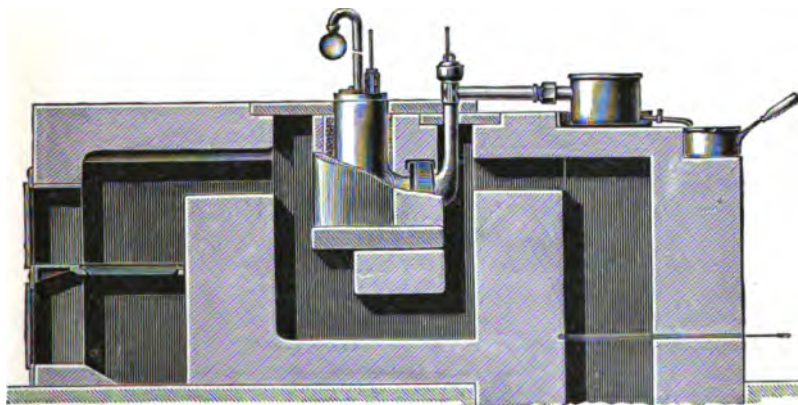
Fig. 36.—Borchers' sodium-reduction plant.

and hot gases without, would rapidly lead to the destruction of the vessel. The decomposition-vessel is, therefore, made to rest on a bridge, and the anode compartment is completely enclosed in a narrow brick chamber filled with powdered charcoal. The manner of withdrawing the chlorine is sufficiently indicated in the drawing.

Disposition of Plant.—The general arrangement adopted in an installation may not appear very economical in respect of electrical conducting wires, but in view of the necessity for a clear space around each separate furnace this could scarcely have been avoided. The annexed scheme (Fig. 37, Plate I.) shows the arrangement of the main conductors, L, which consist of metal rods. Each section of this conductor is connected with the next by a switch, S. From the points marked P conducting wires are led to the anodes, and from

5

those marked N others are connected to the cathodes of the
electrolytic apparatus. The switch, S, is operated in order to
connect up any vessel with the dynamo or to cut the apparatus
out of the circuit again.

Not more than two electrolytic vessels can well be included
in one block, because it is necessary that access may be readily
had to the water-pipes connected with the cooling-rings of the
apparatus; but as these erections do not stand very high this
is no serious disadvantage to the installation. It is not advis-
able to include more than one apparatus in a single heating
chamber, for reasons already explained in connection with the
reduction of magnesium.

Attached to the diagram of the electrical connections on
Plate I., there is given a general plan of the disposition of
dynamo and gas-engine installation, the whole being drawn to
the scale of $\frac{1}{100}$; this is given in order that, at least, an
approximate estimate may be formed of the floor space required
for an installation arranged on the basis of an outturn of about
2 cwts. of sodium in 24 hours. A spare dynamo should be pro-
vided in addition to the two in use, of which each produces the
current for one row of furnaces; this is desirable on account of
the danger to which the melting apparatus is exposed on the oc-
casion of a breakdown. The installation is, substantially, no more
costly if, instead of the three dynamos absorbing 50 H.P. each,
there be used two at 100 H.P., of which one would be always held
in reserve. This single dynamo could then be coupled directly to
the gas engine, in order to avoid all loss of power through belt-
transmission. For the rest, the sketch-plan contains all the
necessary explanations. The switchboard of the three dynamos
may conveniently be placed on the wall of the engine-room;
and the connections are so arranged that each dynamo may be
connected, at will, to any furnace. For the sake of clearness
the connections in this part of the drawing are not laid down to
the actual working scale.

Cost of Electrolytic Sodium-Extraction.—In order to
reckon the cost of a plant adapted to the manufacture of
about 2 cwts. of sodium per diem the following figures may
be taken.

Under favourable circumstances, the electric horse-power
should yield 2·2 lbs. of sodium in 24 hours. Each of the vessels
shown in the sketch is calculated to take 300 amperes, and affords
10 lbs. of sodium in 24 hours. Thus there are necessary for the
installation :—

25 Decomposition-vessels,	.	.	.	.	.	£75	0	0*
Dynamos to furnish 100 electrical H.P.,			.	.		600	0	0
Steam-engines or gas-engine plant with a production of 120 H.P.,								
tion of 120 H.P.,	.	.	.	.	.	2,000	0	0
Cost of building, installation, &c.,	.	.	.	.	.	1,000	0	0
						£3,675	0	0

In order to conduct the process there must be reckoned for, daily :—

7 cwts. salt,	.	.	.	.	.	£0	7	0
3 tons of coal for production of the motive power,						1	10	0
1 ton of coal for the heating of the apparatus,				.		0	10	0
2 firemen,	.	.	.	.	.	0	10	0
2 engineers,	.	.	.	.	.	0	15	0
6 labourers,	.	.	.	.	.	1	4	0
Wear of melting vessel,	.	.	.	.	.	5	0	0
Interest and amortisation,	.	.	.	.		1	14	0
	2 cwts. of sodium therefore cost			.	.	£11	10	0

It is evident that the price of sodium, according to this valuation, cannot be high even if the various items be reckoned at their maximum value. At the present level of prices in Germany (1896) sodium could be produced at from 2 to 3 marks per kilogramme [which is equivalent to 11d. to 1s. 4d. per lb.], and this is cheap as compared with the market rate.

The prospect of sodium being used in the manufacture of aluminium is at present very small; but in addition to the older and well-known applications of sodium two new uses for the metal have lately been found, viz., the manufacture of sodium peroxide and of potassium cyanide.† The former is already largely employed as a substitute for barium and hydrogen peroxides; whilst the use of the latter has been markedly increasing of late owing to the demand for potassium cyanide for gold-extraction processes. Among the older uses of sodium may be mentioned the production of chemically pure sodium hydroxide, the reduction of organic substances in the aniline-colour industry, and the reduction of the compounds of the rarer or more difficultly-reducible elements.

SODIUM ALLOYS.

Use of Sodium Alloys.—The difficulties experienced in the manufacture of pure sodium directed the attention of the electro-metallurgist to the production of alloys which, by reason of the sodium that they contain, might be employed as a substitute for

* [In the German Edition these figures are given in marks. The original prices have here been merely calculated into their English equivalent, the sovereign being reckoned as equal to 20 marks.—Trans.]

† According to Erlenmeyer a cyanide admirably adapted for most technical purposes is obtained by heating potassium ferrocyanide with sodium thus—

$$K_4FeCy_6 + Na_2 = Fe + (4KCy + 2NaCy).$$
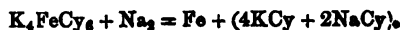
the pure metal.   Of such alloys, those with mercury and with lead have found technical application, and more lately the use of sodium tin alloys has been suggested.

The use of mercury as a cathode in electrolysing compounds of the alkali and alkaline earth metals is a device that was employed by Davy at the beginning of this century, with the object of preventing the difficultly reducible metal from re-dissolving in the electrolyte.   But in spite of this, amalgamation has not been used practically, because the solubility of sodium in mercury is very slight at temperatures below the solidifying point of the resulting amalgam.   But now that the attention of the alkali trade has been turned to the electrolytic decomposition of salt solutions, the formation of sodium and potassium amalgams finds a place in many patents, even if the amalgam be obtained only as an intermediate product which is to be broken up immediately.

Early Apparatus for decomposition of the Alloys.—The first patent of this kind was applied for by Atkins and Applegarth * in 1891 in Germany [in England in 1890], and in other countries; it related to a means and apparatus for the production of alkali- and alkaline- earth- metals and their hydroxides. The method employed consisted in the use of a cylindrical metal cathode, of which the inner surface was amalgamated and kept flooded with mercury during the time of electrolysis.   But the apparatus was so designed that the practical fulfilment of this otherwise excellent idea was out of the question.

The apparatus (Fig. 38), patented in Norway and other countries in 1892, by Sinding-Larsen † for the production of chlorine, alkali- metal amalgams, and caustic alkali showed a substantial improvement on the previous suggestion.   Here two vessels, A and B, are used; of these B is open at the bottom, but is sealed during the electrolysis by the mercury, Q, contained in A.   Through the arched cover of B the carbon rod C is passed into the interior of the vessel, where it serves as anode. The tube X is used to convey the saline solution to the vessel B for decomposition, whilst the side tube of B carries away the chlorine as it is evolved, together with any excess of liquid. The metal, sodium for example, is taken up by the mercury employed as cathode.   If the amalgam be required as such, the mercury in the outer vessel, A, must be covered with a layer of petroleum, but if the process be applied to the production of alkaline hydroxides, water should be substituted for the petroleum.   According to the specification of two later patents ‡ it is advisable to keep the mercury in motion.

* German Patent 64,409 ; [English Patent 20,768, Dec. 19, 1890].
† Norwegian Patent 2925 of 1892.
‡ *Zeitschrift für Elektrotechnik und Electrochemie*, 1894, vol. i., parts 13, 15. [English Patents 14,910, 1893, and 13,499, 1894].

Hermite and Dubose * in their inventions have proposed to utilise amalgams (but in an unpractical manner) as intermediaries in the manufacture of alkali compounds.
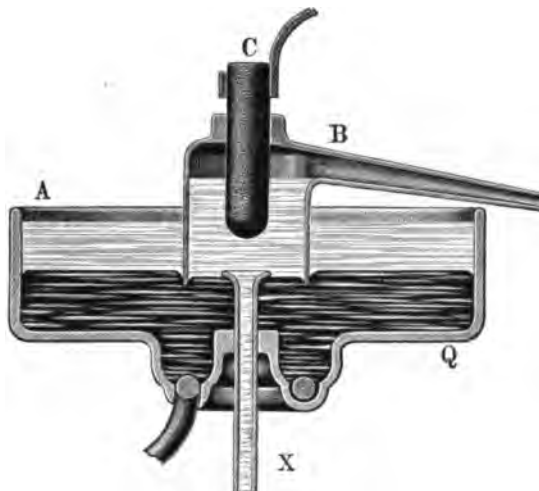
Fig. 38.—Sinding-Larsen's electrolyte cell.

Castner's Caustic Soda Plant.—The idea which forms the basis of Sinding-Larsen's apparatus has been perfected by
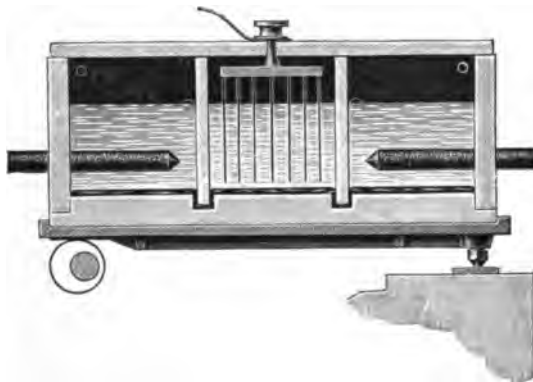
Fig. 39.—Castner's electrolytic cell for the
manufacture of caustic soda.

Castner and Kellner. The oldest of the patents granted to these inventors is that taken out in England by Castner,‡ and

* German Patent 67,851.   † English Patent 16,046, 1892.

illustrated in the annexed sketch ; a supplementary patent was granted in 1893,* and the process is now worked as follows :— The electrolyte vessel is divided by two partitions into three compartments, which are all in direct communication when the vessel is empty by means of wide grooves cut in the floor of the apparatus beneath the partitions. The bottom of the vessel is now covered with a thin layer of mercury. In the middle compartment the cathode, consisting of metal plates, is immersed in water, while in the outer compartments carbon anodes are placed in a solution of salt. Since the partition walls are made impervious to liquids, the course of the electric current is as follows :—From the anode it flows through the saline liquids to the mercury at the bottom of the outer compartments, so that this forms the cathode; it is conducted hence through the sodium-mercury amalgam to the middle compartment, where the amalgam acts as anode and allows the current to pass through the water to the sheet-metal cathode. A gentle oscillating movement is imparted to the whole vessel in order to circulate the amalgam, and thus to facilitate the removal, in the central compartment, of the sodium taken up by the mercury in the outer divisions. With this object in view, the apparatus is supported at one end on a roller or knife-edge standing upon a solid foundation, whilst at the other end it rests upon an eccentric which is rotated by means of shafting. With a layer of mercury $\frac{1}{4}$ in. deep on the bottom of the vessel, the vertical motion imparted by the eccentric should not exceed $\frac{1}{8}$ in. above, and a like amount below, the horizontal.

Later Amalgam-forming Processes.—The same principle has been applied by Kellner † in several forms of his apparatus. He fills small porous cells with mercury, and covers the latter with water. The cathodes are immersed in these cells, which stand between the anodes in a decomposition-vat filled with saline solution.

Although of later date, the apparatus of Vautin,‡ which is based upon the same idea, stands so far behind those previously described that any description of it appears to be unnecessary.

Important as the processes referred to may prove to the alkali trade, they have little or no interest from the purely metallurgical point of view. Alkali metals will never be produced in this manner; and the resulting amalgam contains, at best, so little sodium that it can never be expected to play any other part than that of transporting the metal from the anode to the cathode cell during the time of electrolysis.

* English Patent 10,084, 1893, and German Patent 77,064.
† German Patent 70,007.
‡ German Patent 73,304; American (U.S.A.) Patent 513,661 ; English Patent 2,287, 1893.

The production of the alloys of sodium with lead and tin is of greater metallurgical interest. Although the solubility of sodium in these metals was known, it was not until the year 1889 that an account of the first successful experiments in the production of such alloys was published. Rogers [*] wrote as follows on that date:—"During the last three years (1886-1889) I have experimented on the reduction of sodium chloride, using molten negative electrodes, and especially lead. Lead, tin, cadmium, and antimony all readily alloy with sodium, a large part of which can be recovered from the alloys by distillation in an iron crucible. They can be heated to a higher temperature than pure sodium in acid crucibles without the sodium attacking the crucible. In the following experiments a dynamo machine was used to supply the current. In one experiment a current averaging 72 amperes and 33 volts was passed through molten sodium chloride contained in two crucibles arranged in series for two hours. Each contained 30 lbs. of salts; in the first was put 104 grms. of tin, in the second 470 grms. of lead, each serving as cathode, connection being made through the bottom of the crucible. A carbon anode passed through the cover and extended to within 3 in. of the molten cathode. The crucible containing the tin was nearer the fire, and consequently hotter, and had an average potential across the electrodes of 12 volts, while that containing the lead was 21 volts. When at the end of two hours the carbons were removed, and the crucibles cooled and broken open, the lead was found to contain 96 grms. of sodium, or 17 per cent. There were about 90 grms. of sodium found in the tin alloy, or between 45 and 50 per cent."

The electromotive force used was unusually high, but in the absence of any indications in the paper as to the size of the apparatus, it is not possible to form any idea of the current density employed. This acccount, however, suffices to prove that a practical method for the electrolytic production of lead-sodium or tin-sodium alloys had thus been found. In another paper, Rogers [†] expresses himself somewhat optimistically as to the consumption of power in the extraction of sodium. He expects to obtain from the fused chloride $5\frac{1}{2}$ to $6\frac{1}{2}$ lbs. of sodium per E.H.P. per 24 hours. According to the results already described, such a yield is scarcely to be hoped for; he, however, adds the special restriction, "provided the apparatus is sufficiently durable to permit uninterrupted work during the time."

Vautin then attempted to solve the difficulty of devising suitable apparatus which had thus again become a hindrance to progress.

[*] *Proceedings of the Wisconsin Nat. Hist. Soc.*, 1889 (from Richards' *Aluminium*).
[†] *Journal of the Franklin Inst.*, 1839, vol. cxxviii., p. 486.

His first patents[*] do not call for mention, but his latest speci-
fication[†] must be referred to, because it describes as new an
apparatus[‡] which had been patented in England so far back as
1844. Napier, who was the original inventor, proposed to
separate metals from fused substances, using as cathode a
crucible of some conducting material, which was coated with a
non-conductor (slag) internally down to the bottom. This de-
scription accurately describes the latest form of apparatus
described by Vautin, and illustrated in Fig. 40. But apart from
the absence of any originality in
Vautin's arrangement, this "new"
apparatus, as it is termed in the
patent specification, cannot be dur-
able in character. There is no
material known that could survive
continuous use, even for a few days,
as an insulator in contact with a
portion of the surface of an externally
fired vessel, the vessel being em-
ployed as cathode in a fused mix-
ture of the haloid salts of the alkali-,
earth-, or alkaline-earth-metals. It
may be argued that the lining-
material (magnesia) used by Vautin
is cheap; but even if it cost nothing
it would still have to be rejected,
because it is worthless for use in any
continuous operation, and continuity is essential to the profit-
able application of heat- or electric-energy.

Fig. 40.—Vautin's
apparatus.

Borchers' Plant for Sodium Alloys.—The earliest appar-
atus which the author has successfully applied to the production
of a sodium-lead, or other readily fusible, alloy, is shown in Fig. 41.
The iron melting-vessel, K, consists of a short cylinder termin-
ating in a hollow cone below. The inner wall of the conical
portion is provided with projections, which form terraced
grooves, one above another. The uppermost (and deepest)
groove serves for the reception and melting of the lead,
which is introduced into the apparatus through one or more
funnels. The remaining grooves are intended to intercept the
lead which flows over them, so as to renew its surface as
often as possible, and to enable it to take up a greater proportion
of sodium. For the electrolyte, one of the mixtures of salts
already given may be used in the melted condition. The carbon
anodes, A, with their tube-shaped porcelain shields, C, are hung

* English Patent 13,568, 1893. (*Cf. Zeitschrift für Elektrotechnik und
Elektrochemie,* 1894, vol. i., p. 139.)
† English Patent 20,404, 1893.
‡ English Patents 10,362, 1844; and 684, 1845.

from the fireclay cover, D.   As in the analogous apparatus
described previously, the carbon rods are supported on the
covers, d, by the clamps, V, which also serve to make the neces-
sary electrical connections with the positive leads, P ; the return
leads, N, being connected up with the crucible itself.   The
tubes, R, carry off the chlorine generated during electrolysis,
and the melted alloy which accumulates in the bottom of the
cone overflows by the pipe, X.   The loss of salt which is decom-
posed during the progress of the operation must, of course, be
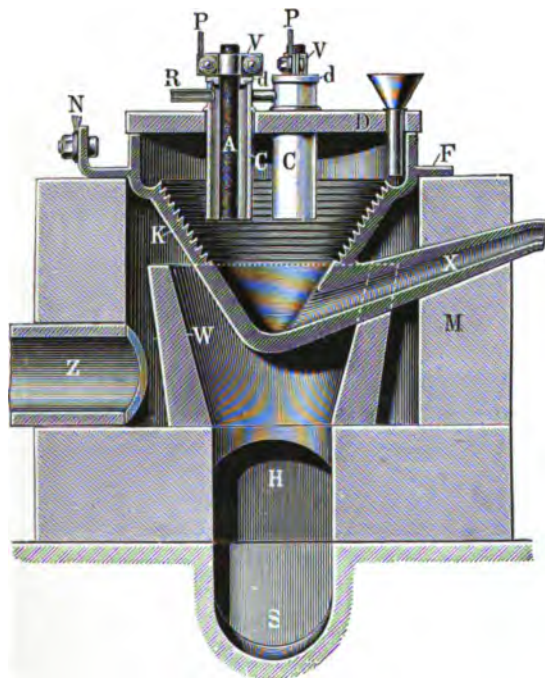
Fig. 41.—Borchers' apparatus for the production of sodium alloys.

made good.   In order to fuse the charge, and to keep it in a
fluid condition, the crucible is suspended by the flange, F, in a
heating-chamber which, in the form here shown, has been found
to be economical of fuel.   A system of side-firing is adopted;
the heated products of combustion entering through the flue, H,
pass into the heating-chamber, and, being deflected upwards
by the circular fireclay baffle, W, return through the annular
space between W and the furnace walls, M, finding an exit by
the flue, Z.   In order to catch any matter that may leak from a
defective pot, a collecting channel, S, is built in front of the fire-

bridge, and from this the material may be run off at will. For small experimental installations, a Fletcher's gas burner may be employed.

This apparatus has since been improved by the removal of the porcelain tubes, which are very liable to breakage and other damage. With this object the upper part of the melting vessel has been raised and surrounded with a cooling ring (Fig. 42). The inner wall of the vessel thus becomes covered with a layer of solidified salt, which protects it from the action of the chlorine evolved on the surface of the carbon electrode.
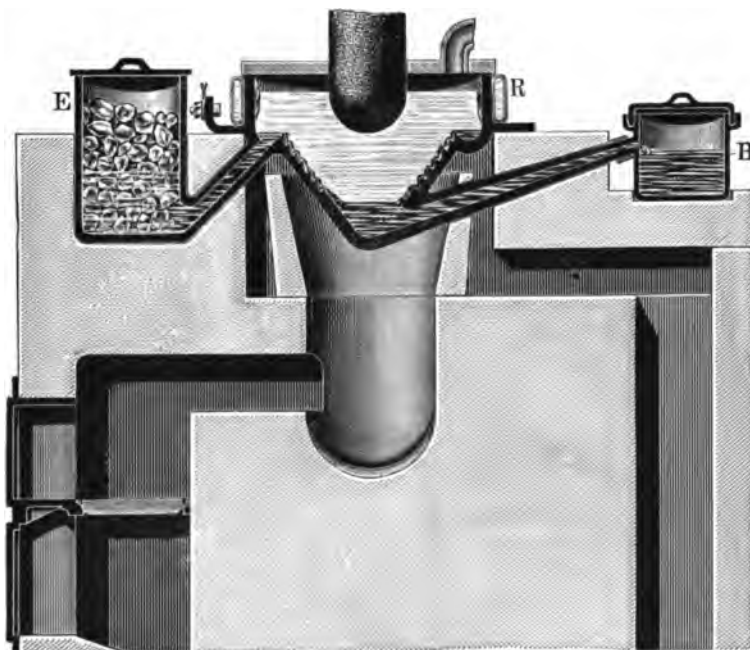
Fig. 42.—Borchers' improved apparatus for the production of sodium alloys.

The lead may be introduced into the uppermost groove of the alloying vessel, either after the manner formerly described or (as here) from a separate melting pot, E, placed above the firing-chamber. The alloying cone is connected by a pipe, leading from the bottom, to a side reservoir, B, which is heated by the waste flue gases. Hence the alloy may be removed for use or for test, as desired. The anode may be made either of one thick carbon rod, or of several smaller rods.

Fig. 42 shows the arrangement of masonry recommended for large installations. A plant of this kind, fifteen times the

actual size of the above illustration, is adapted to a current of 300 amperes, which corresponds to a current-density of about 5000 amperes per sq. metre [3·2 amp. per sq. in.] of cathode surface. The electromotive force required may be only 6 to 8 volts, which is considerably less than that needed for the reduction of sodium in the unalloyed condition. Hence the cost of producing each unit of sodium may be markedly reduced, more especially as the apparatus used for the production of the alloy is both cheaper and more durable than that employed in the extraction of pure sodium.

If a lead alloy containing not more than 10 per cent. of sodium be required, the electromotive force during the whole process need never exceed 8 volts. An estimate of the cost of production may be made, similar to that given on p. 67, by substituting a yield of 3 cwts. of sodium, and a consumption of 9 cwts. of salt for the corresponding entries in the previous table, and by reducing the cost of each apparatus to about one-third. Other easily fusible metals may be used in place of lead; and the application of the alloys are practically the same as those of sodium. Lead, especially, seldom interferes with the reactions for which the sodium is required, but, on the other hand, it frequently checks the superabundant energy of the latter metal.

CHAPTER V.

POTASSIUM.

Properties of the Metal.—Potassium (K ; atomic weight = 39, specific gravity = 0·865) is like sodium, in that it is white and lustrous when freshly cut, but it is softer than that metal, and both its fusing point and its boiling point are lower. It fuses at 62° C., and vaporises between 700° and 750° C., the vapour having a green colour.

Its chemical properties closely resemble those of sodium, but it is usually more violent in its action, and this is especially the case in its reaction with water.

Occurrence in Nature.—In nature it is found only in the form of salts; as halogen salts, in sylvite, KCl, and carnallite, $KCl.MgCl_2.6H_2O$; as sulphates, in the alums, $K_2SO_4.Al_2(SO_4)_3. 24H_2O$; as silicate, in the felspars, $K_2Al_2(SiO_4)_2$, and in mica and numerous other minerals and products of weathered minerals. It appears to play an important part in the life processes of plants and animals ; and both vegetable and animal residues, such as wood-ashes, the ashes of beet-molasses, and the suint from wool-washing are valuable raw materials in the potash industry.

Extraction Processes.—So also, in the same way, the methods of extracting this metal are quite analogous to those in use in sodium manufacture, and it may therefore suffice to refer to almost everything that has been written in the preceding chapter. It should be mentioned, however, that in the direct reduction of potassium carbonate or hydroxide by carbonaceous material, a black porous compound of potassium with carbonic oxide is often found in the retorts and receivers, and this, by reason of its instability has been known to cause serious explosions.

In the absence of sodium, lithium, and magnesium salts, the electrolytic extraction of the metal is effected under almost identical conditions with those observed for sodium, but the bath employed consists of a mixture of the haloid salt of potassium with that of an alkaline earth metal. It will suffice, therefore, to refer to a few methods especially proposed for the extraction of potassium.

Matthiessen's observation[*] that potassium alone resulted from the electrolysis of a mixture of calcium and potassium chlorides was interesting; but the advantages obtained from the reduction in the fusing point of potassium chloride by the addition of the calcium salt are more than balanced by the difficulties which always accompany the electrolysis of mixtures containing calcium chloride.

Linnemann's method[†] depends upon the decomposition of cyanides. The current passes from a carbon plate to a pointed carbon rod immersed in potassium cyanide, which is kept melted in a crucible. If the temperature be so controlled that the upper surface of the bath remains solid, the separated potassium will accumulate under the crust. The high cost of the raw material, however, renders unnecessary any remarks upon the practical utility of the process.

All other processes are already described under "sodium," and reference may be made to them in that chapter.

Uses of Potassium.—On account of the considerable violence of its reactions, the hitherto dangerous method of production, and the high price of potassium salts, the applications of potassium have remained so insignificant that there is practically nothing to be written concerning its use industrially.

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[*] *Liebig's Ann.*, 1855, vol. xciii., p. 277.
[†] *Journ. für prakt. Chem.*, 1848, vol. lxxiii., p. 415.

THIRD GROUP.

CHAPTER VI.

CALCIUM, STRONTIUM, BARIUM.

Properties of the Metals of the Third Group.—The three metals of this group show the greatest similarity in all properties, and therefore also in the methods available for their reduction.

Metal.	Symbol.	Atomic Weight.	Specific Gravity.	Colour.	Fusing Point.
Calcium, .	Ca	40	1·6	Yellow,	800°-1000° C.
Strontium,	Sr	87	2·5	,,	1000°-1200°.
Barium, .	Ba	137	3·75	,,	over 1200°.

Their chemical characteristics are essentially those of the alkali metals. They oxidise and take fire in the air very readily, and with a great evolution of heat, and they show also a strong tendency to combine with the metalloids. Water is decomposed by them at ordinary temperatures with the formation of the corresponding hydroxides. Like the alkali metals they reduce most oxides, including even those of some metalloids—e.g., CO_2, SiO_2, B_2O_3. They precipitate the contained metal from most salts by simple exchange; and, since they decompose water so readily, it is obvious that they must be energetically attacked by acids.

Occurrence of Calcium, Barium, and Strontium in Nature.—The chemical properties of these metals are such that only their salts are found in nature. Among haloid salts the principal is fluor spar, CaF_2; all three metals commonly occur as sulphates: calcium, in gypsum, $CaSO_4 + 2H_2O$, and anhydrite, $CaSO_4$; strontium, in celestite, $SrSO_4$; and barium, in heavy spar, $BaSO_4$; they are often met with as carbonates: in calc spar, marble, chalk, and limestone, $CaCO_3$; in strontianite, $SrCO_3$; and in witherite, $BaCO_3$; and, finally, they may all be

found as phosphates, borates, and silicates, but in these calcium occurs the most abundantly.

Extraction of the Metals.—The separation of the three metals of the alkaline earths from their oxides or halogen salts, is attended with very great difficulty as compared with that of the alkali metals ; and, in spite of some patents recently taken out, it is only practicable on a relatively quite small scale. Davy [*] was the first to accomplish the electrolytic decomposition of the alkaline earths. He formed the moistened hydroxide, either alone or mixed with mercuric oxide, into the shape of a small cup, rested this on platinum foil, which served also as the positive pole, and then poured mercury into the hollow cup of hydroxide, and made this the negative pole. An amalgam was thus produced, from which the mercury could be expelled by heat. According to subsequent investigations, it would seem that Davy did not produce a perfectly pure metal, free from mercury and silicon. Bunsen and Matthiessen, by the decomposition of the chlorides, were the first to prepare the alkaline earth metals in the pure condition. For a long time, fruitless attempts were made in Bunsen's laboratory to electrolyse the chlorides of these metals in the apparatus which had given such good results in the extraction of magnesium ; and these experiments were continued until, in the course of his researches on metallic chromium in 1854, Bunsen discovered the cause of his previous failures. He at that time published the following noteworthy observation,[†] which has since conditioned the success of a large number of electrolytic decomposition :—

" The density of the current used for electrolysis—that is, the relation of current volume to electrode area—exerts a most important influence on its chemical effects. The power of the current to overcome (chemical) affinities increases with this density. . . . Of no less importance is the relative mass of the constituents of the electrolyte through which the current passes."

In the same treatise, Bunsen showed that by using a sufficient current density it is even possible to separate calcium and barium from boiling concentrated solutions of their chlorides, acidified with hydrochloric acid. As negative pole, he used an amalgamated platinum wire immersed in the mass under treatment. The latter was placed in a clay cell, around which stood a carbon crucible, partly filled with hydrochloric acid, and set within a porcelain crucible, the whole arrangement being heated in a water bath. The carbon crucible was used both as anode and as electrolyte cell. Great difficulty was experienced in the electrolysis of calcium chloride by this method, because,

[*] *Phil. Trans.*, London, 1808, p. 335.
[†] *Pogg. Ann.*, 1854, vol. xci., p. 619.

even after a few minutes, the electrode became covered with a crust of lime which interrupted the current. It was, therefore, necessary to lift out the platinum wire, remove the rapidly-dried coating of amalgam, and then re-amalgamate it. Barium amalgam may readily be obtained in quantities of about 15 grains by using crystallised barium chloride, made into a paste with weak hydrochloric acid, at a temperature of 100° C. For these experiments a current density of about 1 ampere per sq. mm. [645 amperes per sq. in.] of cathode surface is necessary.

Matthiessen's Experiments.—As a result of these experiments, Matthiessen,[*] working in Bunsen's laboratory in the year 1855, obtained the metals of the alkaline earths in the pure condition by the direct treatment of the fused chlorides. He writes that : " Although the reduction is easy, it is difficult to obtain the reduced metal in coherent masses, and to separate it from the fused substance. The deposited metals for the most part rise to the surface, by virtue of their low specific gravity, before they have grown to globules of appreciable size; and there they burn so quickly that it is almost impossible to collect them. If the end of the electrode be provided with a bell-shaped attachment of glass or burnt clay, in order to collect the metal, the latter reduces a small quantity of silicon, which separates in the form of a black powder, and prevents the metal from uniting into a regulus."

He proposed three methods of overcoming this difficulty. The *first* method, by which, however, only a very impure metal, or rather an alloy, is obtained, consists in the use of a platinum wire as the negative pole. The alkaline earth metal thus becomes alloyed with platinum, and so acquires a specific gravity sufficiently high to enable it to sink through the fused chloride. After cooling and breaking up the mass the metal is obtained in the form of large grains.

A *second* plan is to melt together two chlorides in simple molecular proportions, by which means a double chloride is produced of so fusible a nature that easily vaporised metals, like potassium or sodium, may be separated in it without volatilising. A porcelain crucible is used for the experiment, and if the temperature be so regulated that a solidified film forms on the upper surface of the mass around the negative pole, this film, on cooling, will be found laden with metallic grains, which may be readily separated from the surrounding material by crushing the whole of the cooled contents of the crucible under petroleum in a mortar. The metal will be visible in the shape of small plates or laminæ amid the pulverised mass.

The *third* way is based on the separation of the metal immediately beneath the surface of the melted chloride by an electrode consisting of a pointed iron wire, which serves to

* *Liebig's Ann.*, 1855, vol. xciii., p. 277.

remove the metal floating on the upper surface as well as that clinging by adhesion to the point of the iron wire. By this method the liberated metal is sufficiently protected from oxidation by a thin varnish-like film of molten chloride to enable the particles to increase to the size of mustard seed.

Extraction of Calcium.—The following method of reduction is exceedingly uncertain in operation; but when successful it is capable of yielding fragments of calcium somewhat larger than a pea. A mixture of two molecular weights of calcium chloride with one equivalent of strontium chloride, and with sal-ammoniac, is melted in a Hessian crucible until the last-named constituent has volatilised; an iron cylinder, to be used as the positive pole, is then placed in the melted salt mixture, and within this is immersed a narrow clay cell, about 4 inches long, previously heated to a red-heat. The clay cylinder is filled with the same fused mixture of salt, and serves for the reception of the negative pole, which may be either an iron wire of about the thickness of a knitting-needle or a carbon rod. If it be arranged that the level of the fused chlorides in the clay cell is about ½ to 1 in. higher than that of the liquid in the crucible, the heating may, with ease, be so regulated that a solid crust forms only on the surface of the liquid in the cell; and the metal will then collect beneath the crust without coming at all in contact with the walls of the cell. With the current from six zinc-carbon elements, such as Matthiessen used in nearly all his experiments, a large quantity of reduced calcium may be obtained after the space of from half an hour to an hour. Only once, however, were a couple of pieces, which had been fused to the size of a pea, obtained by this process; and almost always the metal was found to be distributed in the form of a fine powder in separate parts of the cooled and crushed slag.

Calcium may be obtained in small molten globules more simply and with greater certainty by fusing the mixture in a small porcelain crucible heated, as in igniting precipitates, over a spirit-lamp or between lumps of charcoal, and then passing the current through the electrolyte from a carbon electrode, which should be as large as possible, to a fragment of pianoforte wire only two lines long, which is connected to the negative pole by a stouter wire reaching as far as the upper surface of the liquid. A crust of solidified salt should be allowed to form upon the surface around this wire, which may be removed from time to time (at intervals of three minutes) in order that the crust and metal may be detached in a mortar.

The metal may be reduced in a similar way by so stirring the upper surface of the melted chlorides with the point of the wire for from 1 to 2 minutes, that a glow, produced by the current itself, is observed around the point. Or the point of the wire may, at intervals, be first dipped into the liquid and then raised

until a small electric arc is observed at the surface; this will cause alternations of cooling and strong heating, which should effect the fusion of the metal that has been deposited in pulverulent form.

Calcium is not reduced from its chlorine compound by sodium or potassium. By fusing together one molecular weight of calcium chloride and two of sodium chloride, or equal molecular weights of calcium and potassium chlorides and sal-ammoniac, a double chloride is obtained, which melts at a temperature below the boiling point of either sodium or potassium. If such a [sodium] mixture be electrolysed at a bright red heat with a carbon anode and a pointed iron-wire cathode, a number of comparatively large globules of sodium will be seen to form at the end of the wire (which should only just dip into the liquid) and to rise to the surface, where they will slowly circulate and burn. If such a globule can be removed from the bath, it will be found to contain scarcely a trace of calcium.

Matthiessen was of opinion that if it could be arranged to heat the under part of the crucible containing the mixture $2CaCl_2 + SrCl_2$ to a very high temperature, without fusing the crust on the surface, the calcium might be melted to a regulus below, and this process would then be preferable to any other. These conditions of irregular heating are easily fulfilled by using a crucible of the form recommended for the extraction of magnesium (p. 27), but the fusion of the calcium to a regulus has not yet been accomplished in this way.

Extraction of Strontium.—According to Matthiessen's accounts * the production of strontium appears to be less difficult. A small crucible and a clay cell placed within it are filled with anhydrous strontium chloride mixed with a little sal-ammoniac, so that the surface of the fused mass in the cell may stand at a higher level than that in the crucible. The clay cell is surrounded by a cylinder of iron which serves as the positive pole, and into the cell is dipped a short and very thin piece of iron wire; the latter is fastened to a thicker wire which is enclosed in a pipe-clay tube, reaching as far as the projecting piece of thin wire beneath. If the temperature be so regulated that the mass in the cell is covered with a crust of solidified material, the strontium will collect under the crust (and without touching the side walls) in fragments that may weigh as much as 7 or 8 grains. Barium, however, can be obtained only as a fine powder by a process analogous to this. The statement in Gmelin-Kraut's *Handbuch der anorganischen Chemie* † that Matthiessen had obtained metallic barium in globules the size of mustard seed, adhering to an iron electrode

* *Liebig-Kopp's Jahresbericht*, 1855, p. 323; and *Quart. Journ. Chem. Society*, 1856, vol. viii., p. 107.

† *Handbuch der anorganischen Chemie*, vol. ii., p. 255 (Ed. 1886).

6

by the electrolysis of fused barium chloride, is founded on an error. The sources of information * quoted contain no such statement.

Hiller recommends the apparatus described in the chapter on lithium (p. 35) as specially suitable for strontium reduction. Nevertheless, satisfactory as it has shown itself to be for lithium, it is useless for the production of strontium in pieces of appreciable size. In most cases it will be found, on breaking the crucible, that by far the greatest part of the metal separated at the negative pole has sunk to the bottom, and that it has there reduced the walls of the crucible to silicon and aluminium, or even that it has become re-oxidised at the positive electrode owing to its having been carried forward by the circulation of the liquid caused by the necessarily high current-density used.

The method originated by A. Feldman † must be regarded as retrograde. He proposes either to mix the single or double haloid salts of the alkali- or alkaline earth metals with the oxide of a more electro-positive metal, or else to melt the oxide of the metal that it is desired to obtain with the haloid salts of one (or of several) more electro-positive metals, and then to decompose the fused mixture by means of the current. The metal to be deposited should be present in the electrolyte either as oxide alone, or as haloid salt alone, but not simultaneously in both forms. A sufficient explanation has been given of the disadvantages resulting from the presence of oxides in applying the methods which have hitherto been described for the electrolysis of the fused haloid salts of alkali or alkaline earth metals; and there is consequently no need to re-state the case as against Feldman's process.

Extraction on a Commercial Scale.—It will be gathered from the previous pages that there is no more difficult problem in practical electro-metallurgy than the reduction of calcium, strontium, and barium on a large scale. Yet, on the other hand, almost all the conditions that must be observed in the solution of this problem may be learned from the writings of Bunsen and Matthiessen, by whom they were clearly enunciated. There are necessary:—

1. A high current density (500,000 to 1,000,000 amperes per sq. metre [323 to 645 amp. per sq. in.]).
2. A high temperature at the cathode.
3. A low temperature for the electrolyte.

The first and second requirements may very easily be brought into agreement, but not so the second and third. Yet it is necessary that they shall be fulfilled, for the metal under

* *Liebig's Ann.* 1855, vol. xciii., p. 277; and *Liebig-Kopp's Jahresbericht,* 1855, p. 320.
† German Patent 50,370. [Eng. Patent 9783, July 5, 1888].

deposition must at once be united into masses of considerable size; finely divided metal is very liable to form sub-chlorides, and so, passing into the melt again, to be burned at the anode; a high temperature and a rapid separation of large quantities of metal at the cathode are indispensable, and, as already explained, both these conditions may be fulfilled by applying a high current density at the cathode. But at the same time— and herein lies the secret of the technical difficulty—the electrolyte in the immediate vicinity of the cathode must be kept at the lowest possible temperature, or else the haloid com- pound will redissolve even large globules of metal, and so convey the metal to the anode [as the hypothetical sub-chloride]. The destructive influence of fused and highly-heated alkaline earth salts upon all materials that may be employed in the construction of containing-vessels needs no comment. Without having to read much between the lines, it is possible to find all the necessary suggestions upon these points in the writings of Bunsen and Matthiessen, to which reference has been made so frequently. The very thin iron cathode wire, dipping only just beneath the surface of the electrolyte, must of necessity be strongly heated by any current of high density—and in this way the second of the above requirements is fulfilled. On the other hand, it has frequently been insisted upon that the bulk of the electrolyte should be maintained at a temperature so low that, if possible, a solid crust may be formed on the upper surface. The form of the experimental apparatus described in the original papers, as well as the whole method of applying it, completely excludes the possibility of using such a plant for a profitable installation on the large scale, as, indeed, the authors themselves admitted. At the moment of separation the metal has a very high temperature, and its specific gravity being for the time lower than that of the surrounding salt, it rises rapidly to the surface and is in a great measure burned. This difficulty may be met by using an apparatus such as that first described by Hiller (p. 35). But, unfortunately, the relation between the volumes and weights of the metal and the fused salts is easily altered. As soon as any considerable quantity of metal has separated on the thin wire electrodes and has, in consequence, led to an increase in cathode area, the temperature at this point must necessarily fall. The specific gravity of the metal is thus increased by so much that, before they have time to solidify, drops become detached from the electrodes, and sink through the fused salt; and that which is not dissolved on the way finds an easily reducible silicate (porcelain) when it reaches the bottom. To counteract this evil Borchers has given the cathode the form shown in Fig. 43. Within a wide iron tube with incurved bottom, R, is placed a narrower tube, r, reaching nearly to the bottom. This narrow

tube is used to introduce into R a stream of cold water which, becoming warmed, may find an escape through the tube, S.   At the bottom of the tube, R, and on the outside, is attached an iron pin-like projection, which must be of such a size that it may become heated to a bright red heat by the electric current passing through it on immersion in the electrolyte; it is necessary that it should thus be heated to a temperature higher than that of the surrounding salt.   The tube, R, is sunk to the depth of only $\frac{1}{8}$ to $\frac{1}{5}$ of an inch in the fused mass; and care must be taken that, both before the immersion and during the whole operation, a current of water is circulating through r, so that the bottom of the tube may become coated with an insulating crust of solidified salt, and that the whole of the current may thus be concentrated upon the surface of the projecting pin. The metal, as it drops from the electrode, falls into the iron crucible, T, which is placed beneath R, but is insulated from it.   The copper wire, K, soldered to the upper end of the tube, R, makes the necessary electrical connection with the generator. The bottom of the tube, R, is made concave exteriorly, in order to prevent the escape and subsequent combustion (already alluded to) of the very hot, and therefore relatively light, metal at the moment of production. The incrustation induced by water cooling, and the resulting insulation of that portion of the tube, R, which is immersed in the solution, have for their object the reduction of the conducting area of the cathode.

Fig. 43.—Borchers' experimental apparatus for alkaline earth metal reduction ($\frac{1}{2}$-scale).

As soon as the reduced metal falls from the surface of the pin-shaped cathode, it must be as quickly as possible withdrawn from the active circulation of liquid between the electrodes that results from the high current density employed.   This is accomplished by the use of the crucible, T, which is suspended at a short distance below the negative electrode.   The metal there sinks through the layer of tranquil liquid, protected by the walls of the crucible, and rapidly solidifies at the bottom.

With the dimensions of apparatus shown in Fig. 43, a current of 15 to 20 amperes will suffice for the reduction of calcium or strontium, but 30 amperes, at least, will be required for barium. In the former case an electromotive force of about 20 volts should be used, but in the latter case a pressure of over 40 volts must be available. The yields of calcium, strontium, or barium that may be expected amount respectively to 2, 5, and 1 per cent. of those which should theoretically be obtained; and the mere mention of this low efficiency is sufficient to indicate the extent of the difficulties involved in the reduction. The low quantitative result found in working with this apparatus serves to confirm the suspicion that a considerable portion of the separated metal passes into solution again. If this were due to the collecting-crucible, T, being too warm, a remedy could easily be found. But if the re-dissolving is to be ascribed to the circumstance that the insulated iron parts of the apparatus (wire net and crucible) constitute intermediate poles in the electric circuit, there is apparently but little hope of effecting an improvement in the apparatus.

Borchers' Modified Apparatus.—Bearing in mind all these circumstances, the author has constructed the following appar-
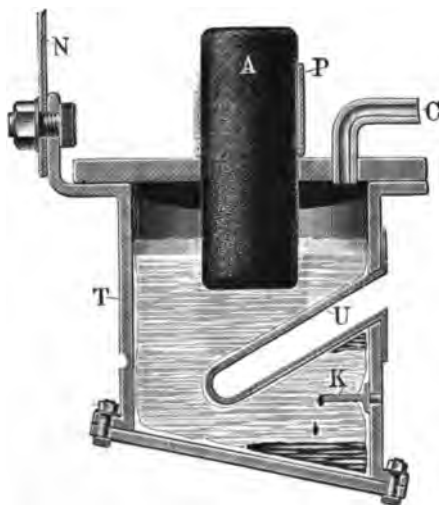
Fig. 44.—Borchers' calcium reducing furnace.

atus (Fig. 44). A wrought-iron crucible, T, is used as the melting vessel; on one side of this is a slot which is provided with a well-fitting iron plate, U, bent into U-shape. Beneath this slot the pins, K, are screwed into the sides of the crucible that they may serve as cathodes. The size of these pins is so arranged

that the current density on every freely exposed surface may be 1 ampere per sq. mm. [about 650 amperes per sq. in.] during the time of electrolysis. The thick carbon rod, A, is used as anode, or a number of thinner rods may be substituted for it if desired. The tube, C, is provided for the removal of chlorine. The method of using the apparatus is as follows:—The fused electrolyte (a halogen-salt of the alkaline earth metal) is first poured into the cold crucible, the carbon anode is then lowered into the salt and the current is switched on as rapidly as possible. The walls of the vessel, T, become covered inside with a crust of solidified salt, and this is maintained throughout the operation by submitting the outside of the vessel, intermittently or continuously, to the cooling action of cold water or air. The crust forms an effective insulator for the internal surfaces of the crucible, and only becomes re-melted on the pins which project some distance into the fused salt. The work of electrolysis begins at once; and the resistance of the bath should be made so great that the action of the current alone may suffice to maintain the electrolyte in a state of fusion. The high current density at the cathode is sufficient to heat the bath in the immediate neighbourhood far beyond the temperature of the surrounding parts. The metal separating here is, therefore, able to unite by fusion into drops, which either fall off, or float upwards, and solidify, therefore, either on the bottom of the crucible or beneath the bent U-shaped plate. It has already been shown that the relation between the specific gravities of the metal and the electrolyte are liable to considerable variation, owing to the changes of temperature that occur. The metal will, therefore, in part sink to the bottom and in part float upwards, according to the conditions of temperature that obtain. By the use of an apparatus such as that shown many of the causes that lead to a loss of metal are obviated, but not all, for the high current density gives rise to a rapid circulation of liquid in the electrolyte, so that much of the reduced metal is carried about in suspension and thus becomes re-oxidised. A part of the metal is also lost, as previously shown, during its passage from the cathode by uniting with the halogen salts to form sub-compounds. The highest yield yet obtained with this apparatus has amounted to only 20 per cent., but this is a distinct improvement upon the 5 per cent. which had previously been the maximum.

Reduction of the Alkaline Earths by Carbon.—The oxides of these metals may be reduced by carbon, the contrary statements to be found in most chemical text-books notwithstanding. By heating the oxides with the right proportion of powdered carbon for the reduction, in an arrangement such as that described on p. 88, a vapour is obtained, which apparently consists of metal and carbonic oxide. Unfortunately, the metal cannot be separated from this vapour, because, in cooling, a

reverse reaction sets in (viz., $Ca + CO = CaO + O$) which cannot be avoided even by operating in an atmosphere of hydrogen. When a large excess of carbon is used, a strongly fritted or fused residue is obtained, consisting of the metals of the alkaline earth employed and carbon.

The possibility of reducing the alkaline earths by means of carbon was confirmed at a later date by the researches of Moissan,[*] who heated mixtures of the oxides or carbonates of these metals in his electric furnace, and thus obtained a residue consisting of the corresponding carbides.

Uses of the Alkaline Earth Metals.—The technical application of these metals has been prevented by their cost, which is necessarily high, in spite of the cheapness of the raw material, by reason of the difficulties encountered in the process of reduction.

CHAPTER VII.

THE CARBIDES OF THE ALKALINE EARTH METALS.

The Production of Carbides.—In treating of the methods to be used in the production of calcium, strontium, and barium, it was stated (p. 86) that the oxides of these metals could be reduced by heating them in admixture with carbon in an electric furnace, and that this process was not capable of affording the metal in a useful condition. By working with an excess of carbon, which is necessary in order to avoid complication of plant, a metallic substance is always obtained that contains much carbon, as in the direct reduction of aluminium; and since this residue has practically none of the usual properties of a metal, it must be regarded as a carbide.

In working with the arrangement first to be described, the author had devoted but little attention to these carbides, because the object that he had in view at the time was the discovery of a practicable method for the production of the pure metals. Meanwhile, the carbides of the alkaline earth metals have become so important, not only in metallurgy, but also in the chemical industries at large, that a closer examination of these products of the electro-metallurgical smelting-furnace will not be out of place here, although they cannot be regarded as metals.

The methods of production industrially available do not yield the carbides in a pure condition, and it is doubtful whether the use of perfectly pure raw materials would give a carbide of quite constant composition. The products obtained from electric

[*] *Comptes Rendus*, 1894, vol. cxviii., pp. 501 and 684.

furnaces of different construction, however, vary but little in
character. A fritted or fused black mass results, that is re-
markable for the readiness with which it oxidises. The carbide
of the alkaline earth metals are decomposed by water or dilute
acids with the evolution of acetylene :—

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$$
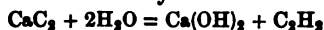
All these carbides exhibit a most powerful reducing (and
desulphurising and dephosphorising) action, which is worthy of
notice in connection with the refining of metals.

Methods of Production.—After Davy,[*] in the year 1836,
had shown that the residue obtained in the extraction of potassium
afforded an evil-smelling combustible gas by contact with water,
and therefore contained calcium carbide, Wöhler,[†] in 1862,
produced a carbide with the formula CaC_2 by the direct union
of calcium and carbon. He heated an alloy of calcium and zinc

Fig. 45.—Borchers' experimental electric furnace.

with carbon, and recommended the resulting product for the
synthetical production of acetylene.

During the year 1880, Borchers succeeded in reducing metallic
oxides, previously held to be unreducible, by means of electrically
heated carbon. When an excess of carbon was employed in the
mixture, the reduced residue was observed to contain much of
this element; but, as stated above, no attention was paid to the
fact, because the object of the research was the production of a
pure metal. The furnace shown in Fig. 45 was employed in
Borchers' experiments with a current of 12 volts and 120 amperes
(= 2 E.H.P.). It is easily put together with the aid of a few
firebricks and carbon rods. A small carbon rod, k, $1\frac{1}{2}$ in.
long, and $\frac{1}{4}$ in. thick, is placed between the two thicker carbon
cylinders, K, which are about $1\frac{1}{2}$ in. in diameter. The thicker
rods are supported between the firebricks, A, B, and C, D,
respectively, in which semi-cylindrical grooves are cut to receive

* *Ann. d. Chem. u. Pharm.*, vol. xxiii., p. 144.
† *Ann. d. Chem. u. Pharm.*, vol. cxxiv., p. 220.

them.   The cables, L L, and the clamps, V V, complete the
electrical connections with the dynamo.   After standing this
simple arrangement upon a firebrick support, and enclosing the
sides by firebricks, as at S, the small space around the narrow
carbon, k, is filled with the required mixture of oxide and carbon,
and the current is then switched on.   An evolution of carbonic
oxide is at once observable, and after a few minutes, the whole
mass situated directly between the poles, K K, will be converted
into carbide.   The remaining unreduced portion serves to pro-
tect the carbide from the action of the air, and from impurities
which would be extracted from the walls of the chamber if
contact were permitted.   The fused or fritted portion, removed
from the furnace after cooling, will be found to evolve acetylene
and other hydrocarbons with great vigour when thrown into water.

Borchers' Electric-Smelting Furnace.—It is unnecessary
to point out that furnaces of the type last described may equally
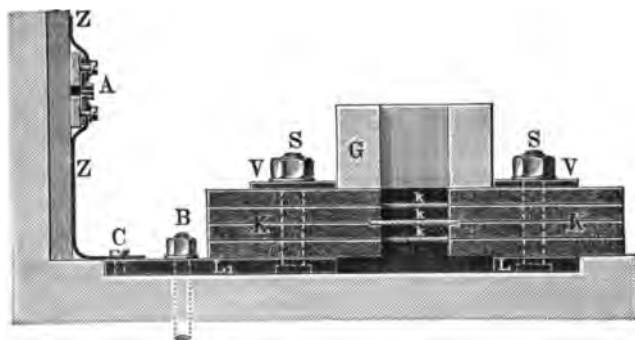
Fig. 46.—Borchers' electric-smelting furnace (longitudinal section).
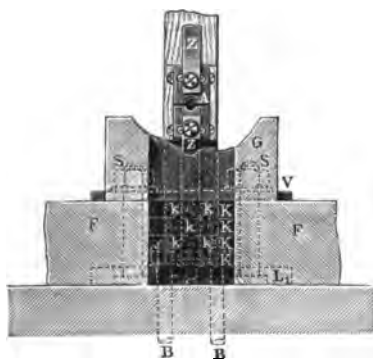
Fig. 47.—Borchers' electric-smelting furnace (transverse section).

well be built on a larger scale ; and as an example of such an
arrangement, the annexed illustrations (Figs. 46 to 48) are

given. They are sketches of a furnace which Borchers has constructed for the research-laboratory of a large firm that is interested in the manufacture of carbides. In these works 20 E.H.P. are available for experiment in the form of a current of 24 volts and 610 amperes.
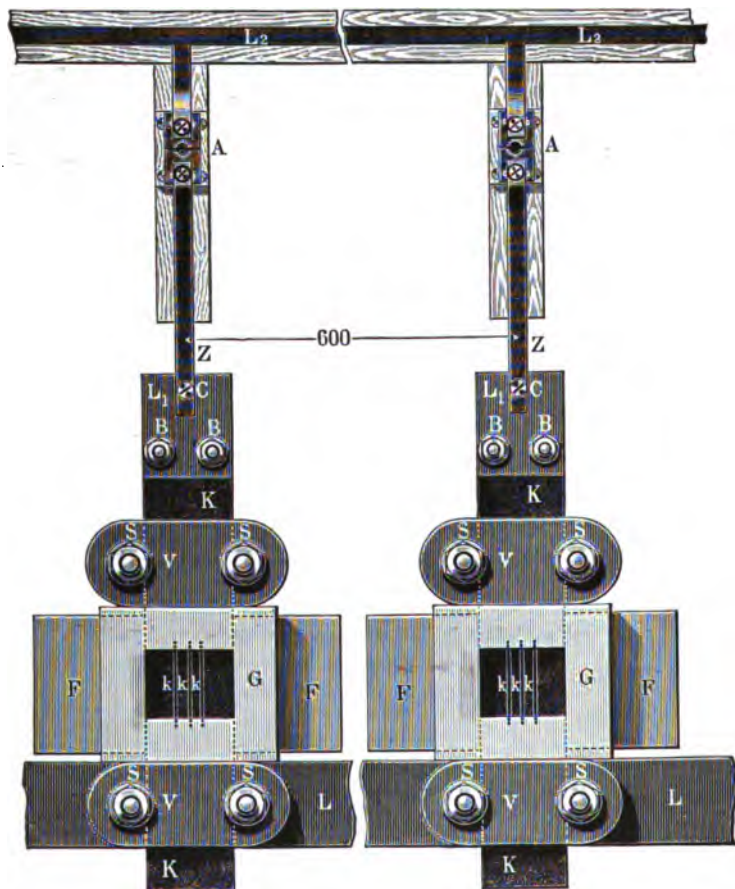
Fig. 48.—Borchers' electric-smelting furnace (plan).

The furnace is shown in vertical longitudinal and transverse section in Figs. 46 and 47 respectively, whilst in Fig. 48* it is shown as viewed from above.

On a stone base-plate, or on a long low block of masonry, are laid the iron or copper conductor, L, which is common to all the

* In this figure is shown the wall to which the conductors, Z and L_2, are attached.

furnaces erected in any given installation, and the separate con-
ducting plates, L_1, kept in place by the holding-down bolts, B, at
the opposite ends of the individual furnaces. The plates, L_1,
can be connected at will with the main leads, L_2, through the
contact screw, C, the switch, A, and the branch mains, Z. The
carbon blocks, K, with the carbon rods, k (each $\frac{1}{8}$ of an inch
in diameter and a little over 3 inches in length), between them,
are attached to the conductors, L and L_1, by means of the screw-
bolts, S, and the clamps, V. The carbon plates thus bound
together form the front and back walls of the furnace, while the
side walls are built of dry-laid fireclay blocks, F. When in
operation a fireclay extension of the furnace, G, above is filled
with a mixture identical with that of the charge, or with coarse
charcoal powder, to prevent access of air.

This furnace is one which may be easily erected or taken
down. In use, the whole space surrounding the coke rods, k, is
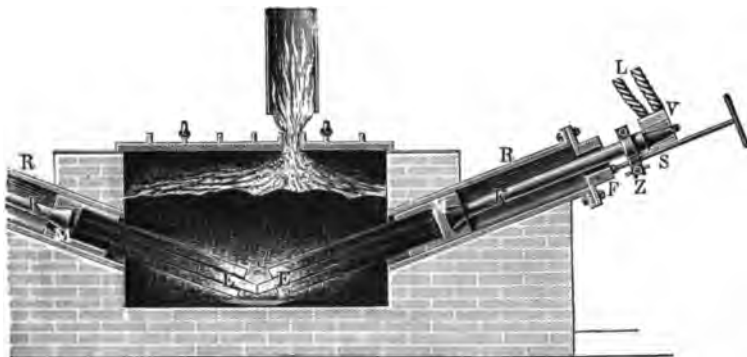
Fig. 49.—Cowles' electric furnace.

filled with the mixture of oxide and carbon, and this is best
effected while the carbon plates, K, and the rods, k, are being
put together. The space between the blocks, G, should, in pre-
ference, be partly filled with an excess of the charging mixture,
and this should then be covered over with powdered charcoal.
A current of 6000 to 6500 amperes per sq. in. (9-10 amperes per
sq. mm.) of total cross-section of the rods, k, should suffice to
give the desired reaction. After about five minutes the main
portion of the contents of the furnace will have been reduced,
and the current is then switched on to a second furnace, the first
being thrown out of circuit.

It is evident, even at the first glance, that the same principle
of construction may be adopted in the largest installations. It
has, indeed, actually been applied by Cowles to the manufacture
of ferro-aluminium and aluminium-bronze on the large scale, as
the illustration of the Cowles furnace (Fig. 49) will at once show.

The detailed description of this furnace will be given in the Chapter on *Aluminium*, in special reference to aluminium-bronze.

Early Experiments in Carbide Production.—The author had established the principles, both of the lime reduction process and of the furnace construction necessary for the reaction, some ten years prior to his publication of the same in 1891 ; only the idea of a technical use for the carbide had not then arisen. The later researches of Maquenne, Travers, and Moissan first recalled attention to this class of compounds.

Maquenne[*] heated a mixture of 26·5 grms. of barium carbonate with 10·5 grms. of powdered magnesium and 4 grms. of wood-charcoal in an iron bottle for four minutes in a Perrot furnace, according to the equation :—

$$BaCO_3 + Mg + C = BaC_2 + MgO.$$
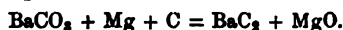
From the resulting amorphous, blue grey, friable product, he found that 100 grms. yielded 5200 to 5400 cc. of acetylene, containing some 0·6 per cent. of free hydrogen. [1 lb. yielded, therefore, about 1500 cub. in. of the gas.]

Travers[†] heated a mixture of sodium, calcium chloride, and powdered retort carbon for 10 minutes in an iron bottle, and obtained a product containing about 16 per cent. of CaC_2.

Following this came the publication of Moissan's account [‡] of the reduction of lime, and, in the presence of a sufficient quantity of carbon, the formation of a calcium carbide, having the formula CaC_2, in his electric furnace. Considering all that had hitherto become known concerning the production of calcium carbide, the fact that it could be prepared in Moissan's furnace was by no means astonishing. The author does not doubt that Moissan will succeed in producing in his furnace many of the reactions which he (Borchers), in 1891, summarised by the general statement that *all oxides are capable of being reduced by electrically heated carbon.* It is strange that in *the year 1894* a patent should have been granted *in Germany* to one Bullier, *for the production of the carbides of the alkaline earth metals,* the patent being based on the fact that *all metallic oxides can be reduced by electrically heated carbon (this having been known since 1891),* and on the supplementary fact, *known since 1862, that calcium will combine with carbon at high temperatures to form calcium carbide.*

Bullier's Specification.—According to Bullier's patent specification § the method of production, which is in accordance with Moissan's published statments, is as follows :—" If a mixture of 56 parts of burnt lime and 36 parts of carbon be heated in an electric furnace of the type known as Moissan's, there will result a definite calcium carbide, corresponding approximately to the

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[*] *Comptes Rend.*, 1892, vol. cxv., p. 558.

[†] *Proc. Chem. Soc.*, 1893, p. 15.

[‡] *Comptes Rendus*, 1894, vol. cxviii., p. 501.   § German Patent 77,168.

composition C_2Ca. By the addition of lime in excess, carbides
of various compositions may be obtained. In the same way, and
with equal facility, the carbides of barium and strontium may be
produced.

"It is obvious that instead of the oxide of the metal to be
employed, the carbonate or any other substances containing the
alkaline earth metals may be used."

After the statement of the author, quoted above as having
been published in 1891, it is open to anyone to produce metals
containing carbon, and
therefore *carbides, by
electrically heating the suit-
able oxides in admixture
with carbon;* and for this
purpose any type of elec-
tric furnace whatever,
whether the author's, or
Siemens', or any other
may be used.

Willson's Process.—
Finally, towards the end
of 1894, Willson, of the
Willson Aluminium Co.,
at Spray (North Carolina),
which had given up the
intention of manufactur-
ing aluminium, appeared
upon the scene with the
statement that he had, in
the year 1893, accident-
ally produced calcium car-
bide in course of his ex-
periments in the produc-
tion of calcium and its
alloys. Doubtless he did
obtain this product; but
it was by the *electrical
heating of a mixture of
lime and carbon,* and that in an apparatus which had been
patented in England and America; for the latter is clearly a
Siemens electric furnace enlarged on the model of the Heroult
furnace. The annexed Fig. 50 suffices to demonstrate this
point. The brickwork, A, surrounds the crucible, B, which is
made of carbon, and receives the charge. This crucible rests
on a metal plate, *b*, by which it is brought in contact with the
electric conductor. Through the cover is introduced a thick car-
bon rod, C, in such a way that an electric arc can pass between
it and the charge within the crucible. The charge consists of a
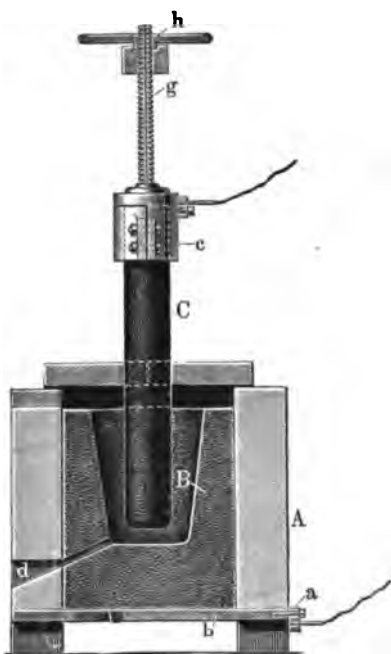
Fig. 50.—The Willson electric furnace.

mixture of lime and carbon, and the apparatus was constructed for use with a current strength of 4000-5000 amperes.

[**The Calcium Carbide Plant at Spray.**—The Willson plant for the manufacture of calcium carbide is in use at Spray, and a larger installation is to be completed at the Falls of Niagara. The furnaces in use in both these places have been described by Morehead and De Chalmot.[*] The present furnace at Spray is in principle the same as that shown in Fig. 50 (above); but the details of construction are very greatly modified. The furnace is a brick vault, divided into two by a partition across the centre. The anode consists of a group of six carbon pencils, each of which is 4 in. square and 3 ft. long; these are firmly clamped in a holder attached to a vertical rod projecting upwards through the roof of the furnace, and supported by a chain, which passes over two rollers, and facilitates the adjustment of the carbons in the furnace. The carbons above the level of the charge are sheathed in a sheet-iron casing. The copper connection with the positive lead is effected outside the vault. The floor of the furnace consists of a stout iron plate, covered with a slab of carbon 8 in. thick, and connected with the negative lead. A flue is provided in the back wall of the chamber, near the top, and the front of the vault is enclosed, when in use, by four iron plates, placed one above the other. The two compartments of the furnace are independent of one another, each having its own electrodes. After charging and regulating the arc in the usual way a current of 1700-2000 amperes × 70-100 volts is employed, and the whole furnace is afterwards allowed to cool before discharging the contents. With the size of anode given above, the current should not exceed 2000 amperes, which would mean a density of about 10 amperes per sq. in. of cross section of carbon. With such a plant, requiring from 150 to 200 electrical H.P., the gross yield of carbide (including a small quantity of slag) is said to vary from 9 to 11·5 lbs. per H.P. per 24 hours. This number agrees with that obtained by Houston, Kennedy, and Kinnicutt,[†] viz., 0·3723 lb. of nett carbide per H.P. hour, which is equivalent to 8·9 lbs. per 24 hours.

In the larger or "King" furnace to be erected at Niagara, several important changes have been effected, as is evidenced by Figs. 50A and 50B, which are taken from Morehead and De Chalmot's paper. The principal modification is the introduction of a movable bottom, in order to facilitate the working of the furnace, a device that has been successfully employed in connection with certain American bloomery furnaces for the manufacture of iron. In this instance the object is to render

* *Industries and Iron*, 1896, vol. xx., p. 322 (from *Journ. of Am. Chem. Soc.*).

† *Progressive Age* (New York), April 15, 1896.

the working of the furnace continuous by withdrawing the hearth as soon as it is nearly full and substituting an empty one, the charge from the former being then covered up until it is cool.   In use, as soon as the empty truck is in place the arc is to be started, and the charge is to be introduced through the side flues, *e*, with the aid of the automatically rotating blades, *f*, without which it would be almost impossible to prevent the
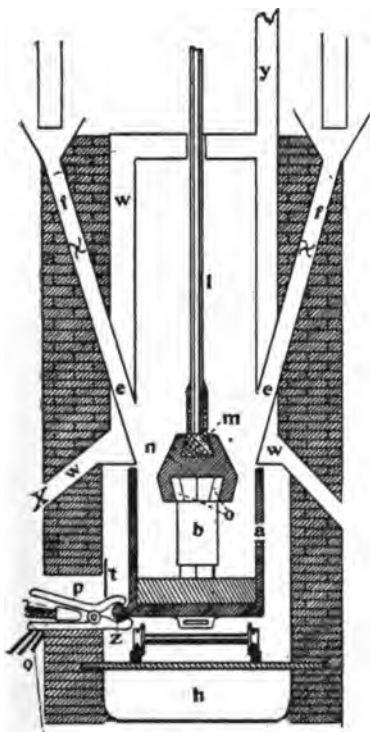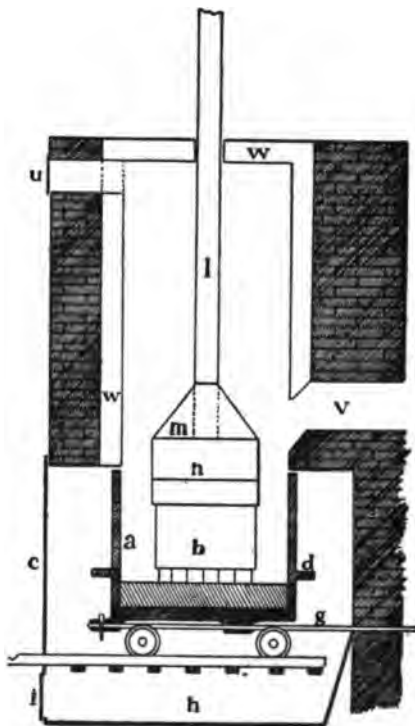
Fig. 50A.   Fig. 50B.
The King furnace for calcium carbide (from *Industries and Iron*).

packing of the finely powdered material in the passages.   The charging is to be effected very slowly, the rate being controllable by the action of the blades, and during the whole time the truck is to be moved backwards and forwards through a space of 2 in., by means of the bar, *g*, at the rate of 20 times to the minute. The reciprocating motion is given with the object of causing the powdered charge to become consolidated and packed in the hearth.   The upper part of the furnace is surrounded internally

by a jacket, *w*, through which cool air is circulated. The door, *u*, at the top is to be kept open until the air in the furnace chamber is displaced by the carbonic oxide resulting from the reaction of the coke and lime; it is then closed, and from that time the flue, *v*, is the only aperture left open.

The bottom of the truck is covered with carbon inside, and the truck itself is provided with trunnions, *d*, by means of which it may be overturned at the end of the operation. A bin, *h*, is provided beneath the hearth to receive the small quantity of charge, which would otherwise be lost, at the moment when the trucks are charged, for the slow charging continues without intermission. The upper electrode consists of 12 carbons, similar to those used in the Spray furnace, gripped in a holder, but with two iron plates, *o*, wedged in between them and the clamp. As the electrodes are heavy, and the temperature in the upper part of the furnace is high, the supporting copper rod, *e* (6 in. by 1½ in.), is strengthened by being placed between two iron bars, each of which measures 6 in. by 1 in. in cross section. The electrical connection with the truck in the furnace shown is made by the clamp, *pz*; but it is preferred to use the rod, *g*, which would then, like the support of the upper electrode, consist of a compound bar of iron and copper.

The above account has been made somewhat full, on account of certain interesting features of the plant, although the records of the experiments with the furnace have yet to appear.—TRANS-LATOR.]

Estimated Cost of Producing Calcium Carbide.—On the basis of the experiments so far made, the cost of producing calcium carbide and acetylene may be estimated as follows, according to American prices :—

11 cwts. of powdered-carbon,	.	.	.	.	£0	12	0
20 cwts. of burnt lime, .	.	.	.	.	0	19	0
202 E.H.P. for 12 hours,	.	.	.	.	1	8	0
Labour, &c., .	.	.	.	.	.	0	12	0
20 cwts. of CaC_2, .	.	.	.	.	.	£3	11	0
20 cwts. of C_2H_2, .	.	.	.	.	.	£8	18	0

For various reasons it is unfortunately not wise to accept these figures exactly as they stand. Some explanaton, for example, is required of the ratio between the lime and the coke-dust used. The reaction takes place according to the equation $CaO + 3C = CaC_2 + CO$, and from this it will be seen that the 20 cwts. of lime will alone require as much as 12·8 cwts. of carbon. It would therefore be interesting to know what class of carbon powder was used if, as the equation indicates, over 16 cwts. of pure coke, charcoal, or anthracite be ordinarily required for the treatment of a ton unit of pure lime.

Then the estimate of 202 E.H.P. would, under the most

favourable conditions, correspond to at least 225 Indicated H.P. To reckon only 28s. for this amount of power applied during twelve hours appears somewhat too sanguine. Finally, passing over the estimated prices of lime and powdered carbon, the item for "labour, &c.," appears to be unduly small.

There is no need, however, to quibble about a few shillings *if the expenditure of power be really no higher than that quoted.* Even if the expenses were doubled, the manufacture of the carbide would always afford a good profit. But, according to the author's experience with this electrical heating process, the power required must be very considerably higher; his results, however, were obtained with dynamos of only 6 H.P., and *there is no doubt that a larger plant would prove more economical.* The author considers that, to make an unbiased estimate of the cost of production, based upon his own small scale experiments, it would be necessary to take the following figures as representing the requirements for the manufacture of 20 cwts. of calcium carbide :—

> 18 to 20 cwts. of quicklime (according to purity) ;
> 16 cwts. of powdered coke, charcoal, or anthracitic coal ; and
> 450˙to 480 E. H.P. for twelve hours.

These numbers do not take into account the labour, apparatus, or other charges involved, and they must not be considered absolute; but they certainly lie within the range of probability. They may, therefore, be regarded provisionally as representing the outside limit of expenditure in the unfavourable sense of the expression.*

* [Very careful experiments were made with the plant at Spray by Houston, Kennelly, and Kinnicutt, who constituted a commission appointed by the *Progressive Age* (of New York) to enquire into the process as it was there applied. Their report was published in that journal on April 15, 1896, and some of their results have already been referred to on p. 94. The estimated cost of production, including all materials, labour, depreciation, stores, and water-power, amounted to $32.767 per short ton of 2000 lbs. (which would be equivalent to £7, 10s. per ton of 2240 lbs.), this estimate being made on the assumption that a plant, turning out an average of 2000 lbs. of gross carbide per diem, was employed, without intermission, day and night, throughout the whole year. They report, however, that both the freight charges for lime, and the cost of coke were unusually high at Spray. And in a later report, Houston and Kennelly have cut down their estimate to £4, 10s. per British ton, on the basis of a production of 10,000 lbs. per diem, with water-power at $5 per H.P. per annum, and with coke at 12s. 4d., and lime at 11s. 3d. per long ton. The assumed cost of the water-power would, however, appear to be based upon a very sanguine estimate; and the Spray factory must be unusually happily placed if they can command power at such a low rate. At Niagara and at Neuhausen, it is commonly regarded as costing in round numbers £2, 10s. (or, say, $12) per H.P. per annum, whilst in a few instances it has been known to exceed twice this amount. Further, as the sources of water-power are taken up, and as the value of falls becomes better known, it seems almost inevitable that the cost—from greater inaccessibility of the falls, or from higher rentals—shall always approximate that of steam-power.—TRANSLATOR.]

7

Use of the Carbides.—As regards the practical applications of the carbides, the probability is that they will be employed in the refining of metals, especially as a deoxidising agent for ingot iron, for it is not easy to imagine a more convenient reducing agent for the molten oxides of the heavy metals. But the largest proportion of the carbide will no doubt be used up at the place of manufacture in the production of acetylene. The future method of operation may consist in decomposing the calcium carbide by water, drying the resulting gas, reducing it to the liquid condition by the united action of cold and pressure, and placing the product on the market in steel flasks, similarly to carbon dioxide, sulphur dioxide, and ammonia. (See foot-note on p. 99.)

Acetylene, C_2H_2, is a colourless gas which has an unpleasant odour [when impure]. It may be condensed to a colourless liquid under a pressure of about 48 atmospheres, and it may some day, therefore, be put upon the market in this form. As bearing upon its use as an illuminant (for admixture with ordinary lighting gas), it must not be forgotten that it is capable of dissolving in an equal volume of water. Alcohol dissolves six times its volume of acetylene. Among other absorbing agents, ammoniacal solutions of cuprous chloride and silver nitrate should be mentioned; from these solutions the gas precipitates $C_2H_2 . Cu_2O$ and $C_2H_2 . Ag_2O$ respectively, each of which substances is insoluble in water but is readily decomposed by acids, with separation of acetylene, whilst each, when in the dry condition, explodes violently under shock or on heating.

Acetylene burns in an ordinary burner with a very smoky flame, but in burners specially constructed to prevent the formation of smoke it gives a high luminosity, *the intensity of the light exceeding that afforded by ordinary illuminating gas in the proportion of 10 : 1*. It is therefore possible that an admixture of acetylene may be used to increase the luminosity of the lighting gas as at present supplied. It is possible, however, that, following upon the solution of the problem of manufacturing the carbide successfully, the makers of illuminating gas will find it advantageous to alter completely the present system of treating coal. In place of submitting the coal to the expensive distillation process, it would be treated in gas-producers or generators, and among these processes that of obtaining producer gas by passing nearly the maximum permissible amount of steam with the air into the producer, would at once come under consideration. This gas has already proved its value for heating purposes and as a fuel for use in gas engines. If, then, this gas, by an admixture of acetylene, can be converted into a good illuminating gas, about which no doubt can be entertained, the works at present engaged in the production of lighting,

heating, and power gas would be employed in making a gas of the above-named description. *A single plant* could thus supply a cheaper gas for heating and power, of which a portion could be mixed with acetylene for illuminating purposes.[*]

Of the other chemical properties of acetylene, the following deserves the attention of the chemical industries. By the agency of platinum black acetylene unites directly with hydrogen to form ethane, C_2H_6. The direct conversion of the acetylene into ethylene, C_2H_4, by the addition of hydrogen is not so easily accomplished as would appear from recently published statements. But the possibility of producing alcohol from acetylene on a commercial scale by the formation of ethylene, the conversion of the latter into ethylsulphuric acid and the decomposition of this into alcohol, depends still upon many questions that have yet to be settled.

[*] [*Note on the Use of Acetylene in the Liquid Form, and as an Enriching Agent for Illuminating Gas.*—It must not be forgotten that acetylene is an endothermic compound, and is, in consequence, very unstable. As compared with ordinary heating or illuminating gas, a far smaller proportion, either of acetylene in air or of air in acetylene, suffices to produce a mixture that may be exploded by contact with a light. But Berthelot has shown that in proportion as acetylene is compressed it becomes more liable to true explosion of itself, without any admixture of oxygen; so that when the pressure exceeds 2 atmospheres, if any portion of the gas were locally heated to its temperature of decomposition, the action would spread through the whole of the gas. Such a result might even be produced by opening a cylinder of the compressed gas too suddenly into a very confined space. Liquid acetylene, when fired by an electrically heated wire, was dissociated so violently that in one case a pressure of over 35 tons per sq. in. was developed ; and, by firing a charge of fulminate of mercury in the midst, the acetylene behaved like a high explosive (such as gun-cotton), shattering the steel flask in which it was contained. It is true that mere mechanical shock failed *per se* to explode even liquid acetylene; but in one instance, in which a cylinder was fractured, the mixture of gas and air became fired by the heat generated by friction between flying fragments of metal, and a violent explosion of the whole resulted. It is obvious that such accidents are likely to occur but rarely, yet the mere fact that there is so considerable an element of danger in connection with the use of acetylene, and that serious accidents have occurred, is likely to restrict the use of the material.

Again, Lewes (*Journal of Gas-Lighting*, 1895, vol. lxv., p. 1067) has shown that although acetylene, when burned alone under favourable conditions, exhibits a luminosity of 240 candle-power (per 5 cub. ft.); yet when mixed with non-luminous (or inferior) gases it does not increase the luminosity in anything approaching to the ratio that it should, according to calculations based upon the proportions of the gases employed. This has been confirmed by Love (*Journal of Gas-Lighting*, 1895, vol. lxvi., p. 339), who found that in an extreme case the luminosity of the acetylene added in small quantity to a large volume of water-gas showed luminosity which, calculated per unit of acetylene employed, was only a little in excess of 5, instead of 230 candle-power. Acetylene is, therefore, hardly likely to come into extended use for the enrichment of illuminating gas in competition, for example, with such a material as oil gas, which may develop an enrichment value of 96 candle-power per unit employed, although, when burned alone, its luminosity is only 60 candle-power.—TRANSLATOR.]

The conversion of acetylene into benzene and higher hydro-carbons by polymerisation whilst passing through a heated tube, is quite out of the question for technical purposes, because the method of producing acetylene can never be sufficiently inexpensive to make it practicable. If all the coke manufacturers were to recover bye-products by using ovens of the Otto or other analogous type, the market would soon be flooded with benzene and other products of the distillation of coal.

Especially noteworthy is the fact that acetylene combines directly with nitrogen under the action of the electric spark to form hydrocyanic acid, $C_2H_2 + N_2 = 2HCN$. It is even possible that under suitable conditions nitrogen might be similarly added to metallic carbides.

Acetylene may be converted into oxalic acid or acetic acid by treatment with oxidising agents in aqueous solution.

From all that has been written in this chapter, it is evident that both the carbides of the alkaline earths and acetylene, the product of their decomposition, deserve the most careful attention. But before far-reaching speculations can be made in this field, it is necessary to determine the cost of production, especially of the calcium carbide. It would be agreeable to find that the estimates made by the author and by Willson were too high. As soon as practical experience in this direction shall have been gained with large installations, the inferences to be drawn will become self-evident.

Finally, as to the locality in which the carbide industries will ultimately be developed, there is no doubt that in the first place the fortunate possessors of water-power will take up the manufacture. But there are many other sources of power unutilised, which at any moment might enter into competition, and among these are especially to be noted iron-works and coke-ovens. The waste gases of the blast-furnace and of the coke-oven at present supply, in most instances, more than sufficient power to drive the whole of the machinery of the works. And the majority of these works are intentionally somewhat extravagant in the installation of their boilers and machinery, in order to get rid of this troublesome profusion of gas. *The surplus energy which passes away unused in many modern works of this description, exceeds not only hundreds, but even thousands, of horse-power units.* There is here open, then, a field which, from the stand-point of national economy, can and will be at once successfully utilised by electro-chemistry. The electro-smelting process adapts itself peculiarly easily to the often varying conditions which obtain in some works, and it will be to the advantage of the iron trade to turn to its own uses the young industry of electro-metallurgy.

PART II.—THE EARTH METALS.

CHAPTER I.

ALUMINIUM.

Properties of the Metal.—Aluminium (Al; atomic weight = 27, specific gravity = 2·6 to 2·74) is the most important of the earth metals. It possesses a white colour and a high lustre, and its fractured surface shows a crystalline structure. It fuses at about 700° C. Its low specific gravity renders it especially useful for many purposes. At ordinary temperatures it shows a remarkable resistance to atmospheric action, and, even at higher temperatures, such as are required for melting and casting operations, the almost imperceptible film of oxide that is formed on the surface protects the metal from further oxidation. Water and dilute organic acids act scarcely at all upon aluminium, but the latter substances begin to attack it slowly on boiling. Nitric acid is almost without action upon the metal, sulphuric acid dissolves it slowly, but hydrochloric acid and caustic soda, on the contrary, attack it energetically. Aluminium precipitates most of the other metals from solutions of their salts, and reduces the majority of oxides when in the molten state, as well as those of carbon, silicon, and boron, the excess of aluminium alloying itself with the reduced substance.

 Occurrence of Aluminium in Nature.—Aluminium is found in nature only in the combined state. All the compounds of aluminium may be derived from the oxide, Al_2O_3, and hydroxide, $Al_2(OH)_6$; from the former are derived the sulphide, Al_2S_3, and the salts which contain alumina as the base; and from the latter the aluminates, which are salts containing the aluminium in the acid radical. Of the compounds that occur naturally, the oxide forms the basis of corundum, sapphire, and emery; the hydroxide is present in diaspore, bauxite, and hydrargillite; and the salts are thus represented :—The fluoride by cryolite; the sulphate by the

alums, alunite, and alum shale; the silicates by the felspars and their products of decomposition, the clays (kaolin, &c.) Among these minerals, corundum and sapphire are used as precious stones, emery for polishing and grinding, and felspar and clay for the manufacture of building-stones, firebricks, pottery, earthenware, stoneware, and porcelain. Chemical processes of a more or less simple kind are employed to utilise alunite and alum shale in the manufacture of alum; cryolite in that of soda and pure aluminium hydroxide and oxide; and the hydroxide in producing the pure oxide and hydroxide; whilst corundum was used in the Cowles process for the direct production of aluminium alloys. None of the minerals can be utilised for the extraction of pure aluminium.

The abundance of natural compounds of aluminium, the valuable properties of the metal, and, finally, the difficulties, which must not be under-estimated, connected with the successful decomposition of the raw material that is present in such abundance, sufficiently explain how it is that the number of researches, of inventions (either actual or merely patented), and of more or less timid suggestions, has become almost interminable. For the better estimation of the value of the processes which have been employed in the reduction of aluminium, it will be desirable to consider separately the different divisions or groups into which, from the metallurgical point of view, they may be classed, viz.:— Precipitation, Reduction, and Electrolytic Processes.

Precipitation Processes of Extracting Aluminium.— Having regard to the scope of this book, a short account of the more prominent processes of this class must suffice, for the precipitation of one metal by the addition of another is an operation which belongs to pure chemistry rather than to electro-metallurgy.

Oerstedt,[*] in the year 1824, was the first to attempt the decomposition of aluminium chloride by means of potassium amalgam, but evidently without result; for other reliable experimenters, working according to his directions, failed to obtain any aluminium. Wöhler,[†] however, in 1827, was successful in reducing the anhydrous chloride by means of potassium. Later, Deville[‡] obviated the difficulties connected with the production and use of aluminium chloride by employing the double chloride of aluminium and sodium instead; and he further substituted the much cheaper metal sodium for the potassium recommended by Wöhler. The process was actually conducted on these lines for thirty years in France (first at Nanterre and later at Salindres), and for a time in

* Oerstedt, *Overs. o. d. Danske Vidensk. Selsk. Forhandl.*, &c., 1824-25.
† Wöhler, *Pogg. Ann.*, 1827, vol. xi., and *Liebig's Ann.*, vol. liii.
‡ *Ann. de Chimie et de Physique*, 1854, vol. xlix. See also H. St. Claire-Deville, *De l'Aluminium*, Paris, 1859.

England also. In 1855 Rose* proposed the substitution of the mineral fluoride (cryolite) for the chloride; and in place of sodium, the use of which had been retained by Rose, Beketofft employed magnesium. But the principal interest at present centres in Grabau's process,‡ which is excellent in all its details. In this process, solutions of sulphate of alumina are first treated with cryolite, in order to obtain the aluminium entirely in the form of fluoride, according to the equation :—

$$Al_2(SO_4)_3 + Al_2F_6 . 6NaF = 2Al_2F_6 + 3Na_2SO_4.$$

The aluminium fluoride, which is insoluble in water, is filtered off, washed, dried, and heated to an incipient red heat, and is then at once charged into a cold vessel lined with pure cryolite. The required quantity of dry sodium, in the form of a cube or cylinder, is now placed upon the hot powder, and the vessel is immediately covered up. The following reaction then occurs, accompanied by a great evolution of heat; but in other respects it proceeds quite quietly :—

$$2Al_2F_6 + 3Na_2 = Al_2 + Al_2F_6 . 6NaF.$$

The aluminium is afterwards found at the bottom of the vessel, melted to a regulus, and covered with a slag of cryolite, which has been completely fused owing to the heat of the reaction. The latter bye-product is available for the production of fresh quantities of aluminium fluoride. Of all the chemical processes, this is the only one which, given a cheap method of producing sodium, is ever likely to come into competition with the electro-chemical methods. The metal obtained by this process has the advantage of being unusually pure.

The Reduction Processes.—For a long time alumina was held to be non-reducible; and even to this day statements to that effect are to be found in the chemical text-books. This has probably resulted from an erroneous comprehension of the fact that pure metallic aluminium in a form that would be useful in the arts is never obtained by the direct reduction of the oxide. In addition to this, the high temperature necessary for reduction can only be (or, at least, is most advantageously) obtained by the conversion of electrical energy into heat. This circumstance has frequently given rise to the assumption that the reduction of aluminium is either entirely or in part due to electrolytic agency. But the production of the metal is really due, as will be shown later, entirely *to a reduction of the oxide of aluminium by electrically heated carbon.*

The idea of heating a material with a high electrical resistance by a powerful current, and of placing this resistance in the most

* *Pogg. Ann.*, 1855, vol. xcvi. † *Jahresbericht der Chemie*, 1865.
‡ German Patent 47,031. [English Patents 14,356, Oct. 21, 1887, and 15,593, Nov. 14, 1887.]

intimate contact with the mixture to be reduced (the material being distributed uniformly through the whole mass and becoming, ultimately, a necessary constituent of such a mixture) unquestionably deserves the most careful attention. It is by no means a new discovery, and if there be occasion for surprise, it is less on account of the results that have followed the application of this principle than because these results have been so tardily effected. For the *Philosophical Transactions*[*] of the Royal Society of so early a date as 1815 contain the first record of the metallurgical application of the heat generated by an electric current in a resistance:—"Pepys . . . bent a wire of pure soft iron so as to form an angle in the middle, in which part he divided it longitudinally by a fine saw. In the opening so formed he placed diamond powder, securing it in its situation by two finer wires, laid above and below it, and kept from shifting by another small wire bound firmly and closely round them. All the wires were of pure soft iron, and the part containing the diamond powder was enveloped by thin leaves of talc. Thus arranged, the apparatus was placed in the electrical circuit, when it soon became red hot, and was kept so for six minutes . . . On opening the wire, Mr. Pepys found that the whole of the diamond had disappeared, . . . and all that part (of the iron) which had been in contact with the diamond was converted into perfect blistered steel. A portion of it being heated red and plunged into water became so hard as to resist the file, and to scratch glass."

Depretz[†] first described a small apparatus, which is still very suitable for many experiments: this consisted of a tube of sugar charcoal rather more than $\frac{1}{4}$ in. wide, and almost $\frac{9}{10}$ in. long. It was closed by two plugs of the same material, and, being placed in the circuit of a powerful electric current, became heated with its contents to a white heat.

Even if the two arrangements just described have no direct reference to the reduction of aluminium, they are, nevertheless, worthy of consideration in connection with certain patent specifications of a later date. The application of this principle to the production of aluminium was first proposed by Monckton[‡] in a patent which he took out in England. A strong electric current was to be passed through a reduction chamber charged with alumina and carbon, in order that the mixture (by the agency of the carbon) might be so highly heated as to lead to the reduction of the earth metal by the carbon. At the time, this process was not practicable, commercially speaking, for the production of aluminium, even if it could have produced a sufficiently pure metal, because no adequately cheap source of electrical energy was available until 1867, when the dynamo was invented. But,

[*] *Phil. Trans.*, 1815, vol. cv., p. 371.
[†] *Comptes Rendus*, 1849, vol. xxix.   [‡] English Patent 264, 1862.

in addition to this, the metal obtained in this way could not have paid for the energy expended; for the absorption of carbon* could not be avoided in this process, and a small proportion of carbon is sufficient to render aluminium useless for technical purposes; a certain loss of metal by evaporation would be inevitable; and, finally, the product of the reduction would be a gray, brittle, crumbling mass, scarcely fused, but just fritted together, and containing, besides aluminium, aluminium carbides, carbon, and other impurities which must inevitably be derived from the carbon used for reduction. Underlying the process, however, there was a perfectly sound principle which has found, and will find again, many valuable applications in its proper sphere in metallurgy.

The Cowles Process.—After a long interval, the Brothers Cowles introduced (in 1884) a process, by which there was made available for use a number of alloys, of which the valuable properties had been in part known for a long time. Considering that the impossibility of producing a sufficiently pure metal by the direct reduction of alumina with carbon has been proved, the invention of Cowles must be regarded as particularly fortunate, for it consisted in alloying the aluminium, at the very moment of its production, with another metal, and so avoiding the absorption of carbon, or at least reducing it to harmless proportions. But without any wish to begrudge to the inventors the recognition that is commonly awarded them, it must yet be noted that their patent specification covered too wide a field. In the principal patent † it is stated that the invention refers to a class of furnace in which the electric current is employed as the sole source of heat. Previous attempts had been made, it was said, to reduce ores and to conduct other metallurgical operations with the aid of the electric arc; but this invention consisted chiefly in the use of a granulated material of high resistance, or low electrical conductivity, so connected in an electric circuit that it formed an uninterrupted part of the same. In consequence of its high resistance, it became red hot, and afforded all the heat required. The substance to be reduced was mixed with this granular material, and thus absorbed the heat at the very place of its production.

* As the existence of compounds or "alloys" of aluminium and carbon has been disputed, reference may here be made to an account in the *Zeitschrift für Electrotechnik und Elektrochemie* (1894, part 6), in which is described a crystallised aluminium carbide, C_3Al_4, obtained by Moissan in the following way (*vide Comptes Rendus*, 1894, vol. cxix., p. 16): 15 to 20 grms. [about ½ oz.] of aluminium were placed in a carbon boat, and enclosed within a carbon tube, which was then heated for 5 or 6 minutes in his electric furnace by a current of 65 volts × 300 amperes. Throughout the heating and subsequent cooling of the apparatus an atmosphere of hydrogen was maintained within the tube. The mass, when cold, exhibited yellow translucent crystals of the carbide.   † U.S.A. Patent 319,795.

The conversion of iron into steel must undoubtedly be re-
cognised as a metallurgical operation.   If then Pepys, in the
year 1815, as shown on p. 104, accomplished such an operation
by using a constituent part of the mixture as a resistance in an
electric circuit, and thus brought it to a red heat by the applica-
tion of a powerful current, while the other constituent of the
mixture was in direct contact with it, he was undoubtedly
working in exact agreement with the specification of the Cowles
patent, published in America seventy years later.   It was by an
application of exactly the same principle that Depretz (p. 104),
in the year 1849, placed a diamond in a tube of sugar-charcoal,
and included this in a powerful electric circuit, with the object
of ascertaining the behaviour of the gem in a neutral atmosphere
at high temperature.   Finally, it might well be claimed for
Monckton that he anticipated the Cowles patent as far as it
refers to the reduction of alumina, by his specification published
in 1862 (p. 104).

These circumstances, however, can in no way be said to
detract from the service which the Brothers Cowles have done
in introducing so simple a process for the manufacture of
aluminium alloys.

Instead of entering minutely into the details of the various
forms of furnace which are specified in the numerous Cowles
patents, it will suffice here to describe a smelting installation on
this system, concerning which detailed accounts have been
published.   This installation, which was put down several years
ago in the factory of the "Cowles Syndicate Company," has
been for some time out of operation.*   A 400 H.P. Crompton's
dynamo gave a current of 60 volts × 5000 to 6000 amperes.
The smelting furnaces were built of fireclay, and were rectangular
in cross-section.   They were arranged side by side in a long
row, but were only put in operation one at a time, while the
others were in various stages of cooling, emptying, or charging.
The current was conveyed to and from the battery of furnaces
by two stout copper bars running horizontally along the whole
length of the plant, and at a convenient height above it, one of
these being above the fronts, the other over the backs of the
smelting chambers.   Running upon each of these rails was a
copper clamp, mounted on wheels, with flexible cables of copper
wire attached to it; the other ends of the cables were also held
together by clamps.   A suitable opening in each of the lower
clamps permitted the latter to be hung upon copper bars,
corresponding in shape to the aperture, by which means electrical
connection could be made with the electrodes.   Every electrode
consisted of a bundle of from 7 to 9 carbon rods, each $2\frac{1}{4}$ in. in
diameter, around which a cylindrical head piece was cast, of
iron (if ferro-aluminium were being produced in the furnace),

* *Industries*, 1888, p. 237.

or of copper (if aluminium-bronze were under manufacture). Into the midst of this head piece was cast one of the copper bars referred to above. The electrodes were introduced into the smelting chamber through suitably laid cast-iron tubes in opposite walls of the furnace. By adjusting a simple screw, the electrodes coúld be moved backwards or forwards, as might be necessary for the regulation of the current. In preparing the furnace for use, the bottom was first covered with a layer of limed wood-charcoal, and then the electrodes were introduced; a frame of sheet iron was next placed in the furnace, and the space within it was charged with a mixture of ore, metal, and charcoal, whilst that between the frame and the walls of the chamber was filled
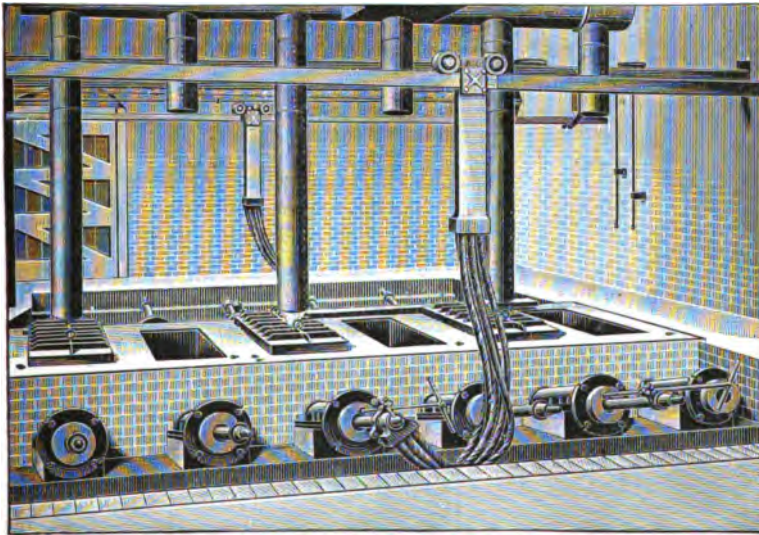
Fig. 51.—Cowles' plant for manufacture of aluminium alloys.

with charcoal only, and the frame was then withdrawn. Some fragments of retort carbon were thrown into the furnace to form a bridge for the current, and, finally, the empty space still left was filled up with charcoal, and the whole was surmounted by a cast-iron cover. In the centre of this cover there was an opening for the escape of gases generated during the smelting operation, the gases were enkindled, and the products of combustion were led through a tube into a furnace in which any alumina that they might contain should be deposited. The melted alloy accumulated on the hearth of the furnace, and was run off through a taphole placed there for the purpose. The slag, which consisted of a very intimate mixture of alloy and charcoal,

was powdered and washed to separate the charcoal, the residual
alloy being introduced into the furnace with a fresh charge.

In the furnace above described, from 15 to 20 cwts. of ferro-
aluminium or aluminium-bronze, containing 15 to 17 per cent.
of aluminium could be produced daily.   The bronze was
remelted with the requisite proportion of copper to yield the
alloys required for the market, containing respectively 1·25, 2·5,
5, 7·5, and 10 per cent. of aluminium, and was cast into ingots
weighing from 10 to 12 lbs. each.   The average electrical power
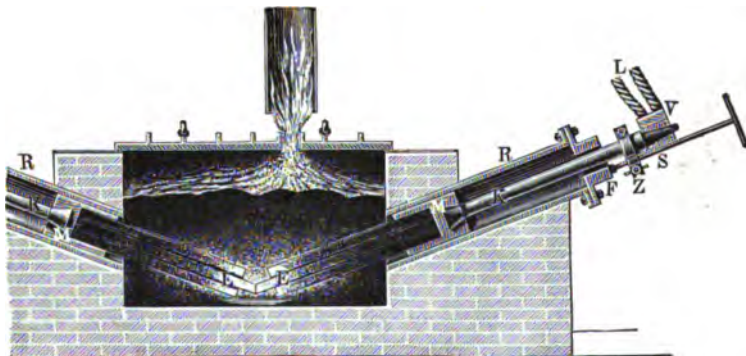
Fig. 52.—The Cowles furnace (longitudinal section).
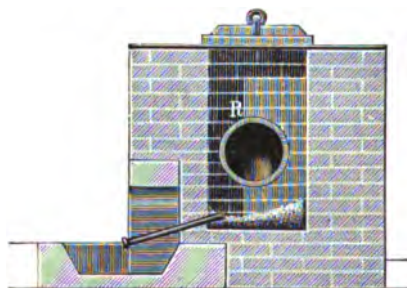
Fig. 53.—The Cowles furnace (cross section).

required amounted to 50 horse-power hours per kg. [which is
nearly equivalent to 23 H.P. hours per lb.] of aluminium.   A
general view of a smelting-house is shown in Fig. 51, whilst Fig.
52 gives a longitudinal-, and Fig. 53 a cross-section of a single
furnace.   In these drawings, E E, are electrodes, consisting of
9 carbon rods, each about 1¼ in. thick, around which are cast the
cylindrical metal blocks, M.   At the ends of these blocks,
opposite to the carbons, the copper rods, K, are introduced.
The whole arrangement slides in the tube, R, and may be moved

in either direction with the aid of the screw, S, and the nut, which forms part of the collar, Z, attached to K. The current is conveyed by the copper wire cables, L, which are gripped by the copper clamp, V; and this in turn is rested on the conical end of the rod, K, which projects beyond the mouth of the tube, R. The cast-iron guide-block, F, serves to keep the rod, K, in place.

Theory of the Cowles Process.—It is evident from an inspection of Fig. 52, which shows the usual arrangement of the carbon rods within the furnace during the operation of smelting, that these rods, so often falsely termed electrodes in descriptions of the plant, are really only resistances introduced into the circuit of a powerful current. It is they which are first heated, and which then impart their heat to the surrounding charge. By degrees the particles of carbon in the mixture form part of the circuit, and so also act as resistances, whilst the rods, E, become partly burned by the oxygen of the metallic oxides.

Hampe * refuses to admit that the heat generated by the current can alone suffice to bring about the reduction of alumina by carbon, because many attempts to reduce alumina by carbon in the presence of copper or copper oxide have given negative results, even though the high temperature of a Deville's furnace was employed. These experiments have led him to the following conclusions :—

"If a temperature nearly equal to the melting point of quartz be insufficient to enable carbon to reduce alumina in the presence of copper, it is certain that the temperature of the electric furnace, although it is much higher than this, will also fail. I believe, therefore, that the production of aluminium-bronze by the Cowles process is dependent far less upon a (chemical) dissociation of alumina in the electric furnace than upon the electrolytic decomposition of the alumina by the current passing through it, the earth being brought into a state of fusion by the electric arc. According to my view, then, the action of the electric arc is primarily electro-thermic, but it is also distinctly electrolytic."

The author cannot agree with this view, but believes, on the contrary, as a result of his observations, that the decomposition of the alumina in the Cowles furnace is attributable *solely to the influence of the heat generated by the current in the resistance that is introduced into the circuit;* and, further, that it is not necessary to employ the higher temperature obtainable by the agency of the electric current in order to bring about the desired result. It is not beyond the range of possibility that even the temperature of a Deville's furnace should suffice for the initiation and completion of the reaction. It is not possible, however, with such an apparatus to fulfil all the conditions that obtain in

* *Chemiker Zeitung*, 1888, p. 391.

the electric furnace. For if a charge be placed in one or, as in Hampe's experiment, two crucibles, and be then submitted to the very high temperature of one of the best of these ordinary furnaces, the heat of the surrounding fuel will be imparted but slowly to the mixture enclosed in the crucibles. The temperature of the charge, therefore, rises quite gradually to the melting point of copper or the reduction temperature of copper oxide, and long before the alumina and carbon shall have attained the temperature at which aluminium could be produced, the copper will have liquated out more or less from the mixture. The evolution of heat from the union of copper with aluminium, that Hampe had hoped would favour the reaction, cannot occur until some free aluminium has been actually produced.

The conditions in the Cowles furnace are quite unlike those just described. In this case, one of the charge constituents that is to take part in the reaction—viz., the carbon required for the reduction—is almost instantaneously raised to a temperature which, as will be seen from an experiment shortly to be mentioned, is amply sufficient for the reduction of the alumina. Copper or copper oxide is not essential to the reaction, but is added simply with the object of obtaining the aluminium in a serviceable form as an alloy, since without this addition the aluminium would combine with a portion of the excess carbon to form a completely useless material, which no subsequent refining operations would purify.

Thermal Reduction of Alumina by Carbon.—The author's assertion may be proved by the following experiment (Fig 54) :—
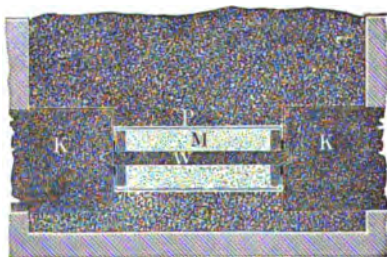
Fig. 54.—Arrangement to show direct reduction of alumina by carbon.

A thin carbon pencil, W, about $\frac{1}{8}$ in. wide and $1\frac{1}{4}$ in. long, is fixed between two stout carbon rods, K, about 1 to $1\frac{1}{2}$ in. in diameter. This pencil is passed through a small paper bag, P, about $1\frac{1}{2}$ in. in length, filled with an intimate mixture, M, of alumina and carbon. The mixture is prepared by repeatedly mixing and heating aluminium hydroxide with tar. The ends of the paper cartridge are closed by small cork plates, and the whole is packed in coarse charcoal powder. The electrical

connections are now made, and a current of 35 to 40 amperes is passed through the arrangement for from two to three minutes. After the cartridge has cooled sufficiently, the charcoal powder is removed, and the carbon pencil will be found surrounded with a fritted mass, which, on examination, will prove to be aluminium containing a considerable proportion of carbon. The possibility of an electric arc having been formed is excluded by the conditions of the experiment, and, in the absence of any break in the conducting circuit within the charge mixture, the occurrence of electrolytic decomposition is also negatived. It is unnecessary to point out that an admixture of copper or copper oxide with the charge would have led to the production of aluminium-bronze. With a simple arrangement of the above type it is, therefore, easy to test the validity of the assertion previously made, that *given a sufficiently high temperature all metallic oxides are capable of being reduced by carbon.*

As above explained, it was necessary, in order to produce the temperature required for the reduction of alumina, to pass a current of 35 to 40 amperes through the $\frac{1}{8}$ in. carbon pencil; this is equivalent to 5 to 6 amperes per sq. mm. [3200 to 3800 amps. per sq. in.]. A current of 10 amperes per sq. mm. [6500 amps. per sq. in.] will suffice for the most difficult case, and should yield a temperature which, under these conditions, will effect the reduction of any metal.

The electromotive force required to overcome the resistance of such a carbon pencil, $1\frac{1}{4}$ in. long, with the production of a current ranging between the above-named limits of density, would be 10 to 17 volts. With the aid of these data it is easy to construct a resistance that shall be suitable to the current employed in any given experiment. It must, however, be pointed out that an attempt to work with a smaller current than that named above will lead to great inconvenience and many derangements of plant, because very thin carbon pencils are easily broken, and may become burned through by the oxygen of the metallic oxides within the first minute of use, even in presence of an excess of carbon in the surrounding mixture.

Tests made with the most varied descriptions of carbon rods, such as are used in arc-lamps (pencils $\frac{1}{8}$ to $\frac{1}{4}$ in. thick being specially made for this purpose), have led to the adoption of the following average numbers as sufficiently accurate for general calculations :—An electromotive force of 0·3 to 0·4 volt is necessary to drive a current of 1 ampere through 1 mm. of a carbon pencil at the temperatures of these experiments, with a current density of 6 to 10 amperes per sq. mm. [4000 to 6500 amperes per sq. in.] of sectional area.

Modified Borchers' Resistance Furnace.—Reference may here be made to certain forms of apparatus which the author has constructed, upon the principle of that described above, and

for experiments in this direction. They vary only in the arrangement of the so-called armature. One of the simplest

forms is that shown in Fig. 55. The plumbago crucible, T, contains the mixture of oxide and carbon, O, and at the same time forms one of the electrodes. The thick carbon rod, K, forms the other electrode, and between them is the thin carbon pencil, W. The firebrick, S, perforated in the centre, acts as a cover to the crucible and as a guide block to the rod, K. The copper clamps, C, and the copper wires, D, convey a current to the apparatus sufficient to bring the rod, W, to the required temperature.
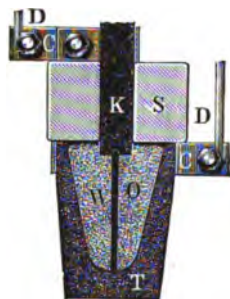
Fig. 55.—Modified experimental Borchers' furnace.

Two other forms of the apparatus * are shown in Figs. 56 to 58. In the former (Figs. 56, 57), a cast-iron crucible holder is used; this consists of a base plate, F, with a block, B, firmly fastened to, or cast in one piece with, it. There is also a second movable block, S, which may be
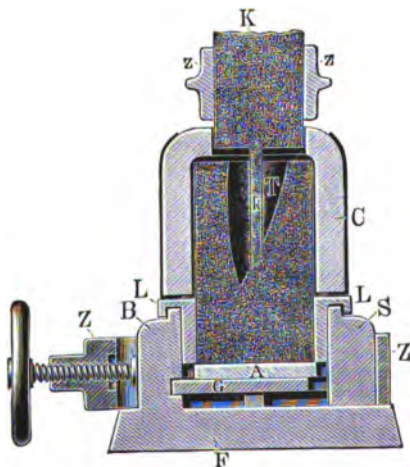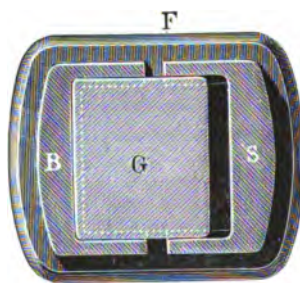
Figs. 56. Fig. 57.

Modified Borchers' furnace in section, and in plan.

drawn close to B by means of a screw or spring, and the wrought-iron band, Z. A groove is cut in each block to receive the small iron plate, G. This arrangement serves the

* Borchers', "Proben," in *Zeitschrift für angewandte Chemie*, 1892, p. 133.

double purpose of giving support to the crucible, T, and of acting as a guide to the block, S, when it is caused to approach B. If necessary, by reason of the crucible being too short, a plate of fireclay or asbestos, A, may be placed between G and the crucible. Under certain circumstances, it is possible to use the same crucible several times, if at least it be made of a good dense carbon or graphite, because the solidified charge may generally be loosened and extracted from it very easily without any appreciable damage to the inner surface ; and the exterior can never be attacked, because the heating of the charge proceeds from the centre outwards. It is, therefore, only necessary from time to time to cut or grind away such portions of the top of the crucible as have become burned or chipped, and to deepen the cavity somewhat by means of a suitable boring tool.

In order that it may not be necessary to use a separate holder for every different shape or size of crucible, the loose collar, L, is used, shaped to correspond with the outer form of the crucible, and made of some metal that is a good conductor of electricity. These are made in two parts like the bearings of shafts, or plummer blocks, and are simply hung within the cheeks, B and S. The other parts of the apparatus—namely, the fireclay jacket, C, the carbon rods, K and k, and the carbon-holder, z—correspond exactly with the similar portions of the furnace shown in Fig. 55, and therefore require no further description. Fig. 56 shows the apparatus in vertical section, with the omission of a few unimportant details ; Fig. 57 is a horizontal section through the crucible holder, with the band, Z, removed. From the two figures, the use of G as a guide for the two plates B and S can be clearly made out.

Finally, Fig. 58 shows a crucible support which the author has devised to take crucibles of different diameters, provided that the variation be not too great. The screw, S,

Fig. 58.

Borchers' support for crucibles of different diameters.

is let into the base plate, F, the nut, M, is provided with channels in its circumference, into which the springs, E, made of metal plate

8

about $\frac{1}{32}$ in. thick and $\frac{1}{5}$ in. wide, are clamped by the ring-shaped wedge, R. The number of springs required will depend upon the diameters of the nut and the crucible; but to ensure good contact with the carbon crucible, not fewer than eight should be employed. Over the springs is passed a sheet-iron ring, O, which is proportioned to the size of the crucible, so that by using different rings the apparatus may be adapted to various sizes of crucible. The metal ring, P, which is in connection with one pole of the electric generator, is screwed over the spindle, S, before the crucible clamp is put into position. The remaining letters, T, K, k, C, z, indicate parts corresponding to those similarly lettered in Figs. 56 and 57.

The manner of using these holders is ordinarily as follows :— The thin carbon rod is first placed in the crucible, then the charge is introduced and pressed down gently, the fireclay jacket is next dropped over the crucible, and, finally, the thick carbon rod is brought into intimate contact with the smaller pencil by the application of a gentle pressure. The electric circuit may then be closed. By the employment of any of the ordinary simple forms of regulator, it is possible to reduce the current, and therefore the heating effect, instantaneously from the maximum to practically *nil*; or it may be varied at will between these limits.

THE ELECTROLYTIC METHODS OF REDUCING ALUMINIUM.

Electrolysis of Aqueous Solutions.—In order to trace without interruption the history of the development of the only electrolytic methods that are technically practicable, it is desirable to consider separately a whole class of impracticable inventions, which pretend to effect the electrolysis of aqueous solutions.

The electrolysis of aluminium salts in aqueous solution, or in solvents which contain hydrogen and oxygen, always affords hydroxides and never the metal. In spite of this well-known fact, inventors are found here and there who profess to have obtained the metal under ordinary circumstances by the direct action of the current upon aqueous solutions of aluminium salts; but the author, after many experiments in this direction, is led to the conviction that they have by some chance fallen into error. In many instances it can be proved, almost with certainty, that some metal, other than aluminium, has been deposited; and it is in these cases easy to discover the source of the metal which, in some of its properties, closely resembles aluminium or an alloy of that metal. Nevertheless, a short account will be given of some of the proposals that have been patented or otherwise

brought before the public. The earliest records in this subject consist of two English patent specifications.

Thomas and Tilley* claimed to electrolyse aqueous solution of freshly precipitated aluminium hydroxide in potassium cyanide.

Corbelli† proposed the use of an electrolyte containing 2 parts of aluminium sulphate or alum, with 1 part of calcium chloride or common salt, dissolved in 7 parts of water. The anode was to be mercury (!), the cathode zinc.

The first August number of *Dingler's Journal* in 1854 contained the following report, accompanied by a criticism that was by no means flattering :—

"Reported Process for the Coating of Copper with Aluminium and Silicon by Galvanic Means.—To obtain the aluminium, I boiled an excess of dry hydrate of alumina in hydrochloric acid for one hour, then poured off the clear liquid, and added to it about one-sixth of its volume of water ; in this mixture I placed an earthen porous vessel containing one measure of sulphuric acid to twelve measures of water, with a piece of amalgamated zinc plate in it. In the chloride of aluminium solution I immersed a piece of copper of the same amount of immersed metallic surface as that of the zinc, and connected it with the zinc by means of a copper wire, and set it aside for several hours ; when on examining it I found it coated with a lead-coloured deposit of aluminium, which, when burnished, possessed the same degree of whiteness as platinum, and did not appear to tarnish readily by immersion in cold water or in the atmosphere, but was acted upon by sulphuric or nitric acid, either concentrated or dilute.

"I found that if the apparatus was kept quite warm, and a copper plate much smaller than the zinc plate was used, the deposit appeared in a very short time, in several instances in less than half a minute. Also, I found that if the chloride solution was not diluted with water, the deposit was equally, if not more, rapid.

"I have also succeeded in obtaining a quick deposit of aluminium in a less pure state by dissolving ordinary pipeclay in boiling hydrochloric acid, and using the supernatant clear solution undiluted with water in the place of the before-mentioned liquid. A similar deposit of aluminium was also obtained from a strong aqueous solution of acetate of alumina ; likewise from a saturated aqueous solution of ordinary potash alum, but rather slowly ; with each of the solutions named, the deposit was hastened by putting either one, two, or three small Smee's batteries in circuit.

"To obtain the deposit of silicium, I dissolved monosilicate of potash (formed by fusing together 1 part of silica with 2¼ parts of carbonate of potash) in water, in the proportion of 40 grs. to 1 oz. measure of water, proceeding in like manner as with the alumina solutions, the process being hastened by interposing one pair of small Smee's battery in the circuit. With a very slow and feeble action of the battery, the colour of the deposited metal was much whiter than that of aluminium, closely approximating to that of silver ; its other properties I have not yet had time to examine" (*George Gore,‡* Birmingham.)

" The author remarks that the aluminium deposited upon the copper plate dissolved even in dilute sulphuric or nitric acid ; but the aluminium produced by Deville exhibits a totally differ-

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* English Patent 2756, 1855.   † English Patent 507, 1858.
‡ *Phil. Mag.*, 1854 (March), p. 227.

ent behaviour. The properties ascribed by Mr. Gore to his metal are insufficient to identify it as aluminium; the same may be said in regard to his silicon. The metallic coating, which was found upon the copper plate in both instances, is probably nothing but zinc, reduced from the zinc sulphate that had formed in the porous clay vessel at the expense of the dilute sulphuric acid and the anode (zinc plate). (*J. Nickles.*) [*] "

Jeanson[†] electrolysed solutions of an aluminium salt of 1·15 to 1·16 specific gravity, at a temperature of 60° C.

Haurd[‡] recommended an aqueous solution of cryolite in chloride of magnesium or manganese.

Bertram[§] wished to separate the metal by a strong current from solutions of aluminium-ammonium chloride.

J. Braun[||] (Berlin) proposed to obtain aluminium by the electrolysis of an alum solution of 1·03 to 1·07 specific gravity at the ordinary temperature. The sulphuric acid liberated during the reaction was to be neutralised by alkali; and the separation of alumina was to be prevented by the addition of a non-volatile organic acid.

According to a patent by Overbeck and Niewerth,[¶] an aqueous solution, either of organic salts of aluminium, of mixtures which afford such salts, or of aluminium sulphate with the chlorides of other metals, is to be electrolysed.

The last part of the foregoing patent is also claimed by Senet[**] in his specification as his invention. He recommends the moderate current of 6 to 7 volts × 4 amperes.

Next, A. Walter[††] appears with a patent, according to which the production of aluminium is possible under the following circumstances:—A solution of aluminium nitrate is to be so decomposed with *a small current density*, but using the current *from a powerful dynamo*, and employing a platinised copper plate, that aluminium may be deposited on the cathode in a pulverulent form.

About the time that this patent was published, in the year 1887, there appeared a recipe from the pen of Reinbold[‡‡] for the production of aluminium deposits on other metals: 50 parts of alum were dissolved in 300 parts of water, 10 parts of aluminium chloride were added, and the mixture was heated to 93° C. After cooling, 39 parts of potassium cyanide were mixed with the solution. With an aluminium plate as anode, and, with a

[*] *Journ. de Pharmacie*, 1854 (June), p. 476.
[†] *Annual Record of Science and Industry*, 1875. *Vide* Richards' *Aluminium*, 1890.
[‡] U.S.A. Patent 228,900, June 15, 1880. *Vide* Richards' *Aluminium*, 1890.
[§] *Comptes Rendus*, 1876, vol. lxxxiii., p. 854.
[||] German Patent 28,760.   [¶] English Patent 5756, Dec. 15, 1883.
[**] *Cosmos les Mondes*, 1885. (From Richards' *Aluminium*, 1890.)
[††] German Patent 40,626.   [‡‡] *Jewellers' Journal*, 1887.

weak current, a good polishable aluminium deposit was to be obtained at the cathode. Even if this process had not been given as a method for the production of aluminium, yet, had it been workable, it would have afforded proof that the metal could be precipitated from aqueous solution. This special case cannot, however, be taken as controverting the statement made at the beginning of this section.

R. de Montgelas,* in the first place, separated the iron electrolytically from a solution of aluminium chloride, and, after adding lead, tin, or zinc oxide, claimed to deposit the aluminium in conjunction with the added metal.

According to the specification of Falk and Schaag,† the aluminium salts of non-volatile organic acids in aqueous solution are to be mixed with the cyanides of copper, gold, silver, tin, or zinc, and after increasing the conductivity of the resulting bath by the addition of alkaline nitrate or phosphate, the corresponding alloys are to be separated from it by electrolytic means.

Burghardt and Twining possess a number of patents which have for their object the production of aluminium and its alloys by the electrolysis of alkaline aluminates. After the addition of cyanides, or of other compounds of an alkali and a metallic oxide, aluminium, or one of its alloys (according to the nature of the added salt), is to be deposited by the current at a temperature of about 80° C.

Nahnsen and Pfleger's‡ invention consists in a separation of aluminium, aluminium-alloys, and magnesium in coherent form, which is to take place without the occurrence of secondary reaction, if (in contrast to the methods usually employed) the electrolyte be cooled, and any rise in the temperature of the aqueous solution during electrolysis be guarded against by the use of cooling agents. Thus, at a temperature of 40° C. a separation of aluminium hydroxide occurs in considerable quantities, but at 40° C. all the aluminium is said to be obtained in the metallic state.

Rietz and Herold§ consider a solution of aluminium, starch, and grape-sugar to be a suitable electrolyte for the deposition of aluminium. After describing the manner of producing this solution, they state that the aluminium separates out, but always in a spongy form, by applying a strong current and using platinum electrodes. The metal is to be subjected to strong pressure, and then to be cast into bars, whilst the residual solution is to be treated for the recovery of the grape-sugar.

The American‖ and German¶ journals record the application of aluminium-plating to iron constructional work at the works

* English Patent 10,607, Aug. 18, 1886.   † German Patent 48,708.
‡ German Patent 46,753. [English Patent 8,552, May 23, 1889.]
§ German Patent 58,136.   ‖ Iron Age, 1892, Feb. 25, June 2.
¶ Stahl und Eisen, 1892, Nos. 7 and 14.

of the Tacony Iron and Metal Company, in Tacony, Pennsylvania, but without describing the most important part of the whole process from the electro-metallurgical point of view—viz., the method of depositing the aluminium.

It is needless to criticise the individual processes here described. The opening statement can only be confirmed that there is no hope whatever that any laurels are to be gained by an attempt to obtain aluminium by the electrolysis of aqueous solutions. The successful extraction of aluminium, in the state of our present knowledge, can only be accomplished by the electrolysis of fused compounds of aluminium.

Early Experiments in the Electrolysis of Fused Compounds of Aluminium.—The first experiments in the production of aluminium were concerned with the electrolytic decomposition of the oxide, but were unsuccessful. They were made by Davy* in the year 1807, after he had succeeded in decomposing the alkaline hydroxides by the same process. The alumina resisted the action of the current which Davy had at his command, but it is not improbable that later experiments† afforded him an alloy of iron and aluminium. Working with a vessel charged with an atmosphere of hydrogen, he employed the following arrangement :—A platinum plate was connected up to the positive pole of a voltaic battery containing 1000 couples. This plate carried a layer of alumina moistened with water and kneaded closely together. Into the upper part of this mass was introduced an iron wire which was joined to the negative pole of the battery. The wire became instantaneously heated to a white heat, and fused at the point of contact with the alumina. The metallic mass, after cooling, was both whiter and more brittle than iron. On treating it with acid a solution was obtained from which alumina could be afterwards separated.

Bunsen‡ was the first to accomplish the electrolytic separation of aluminium from its fused compounds, using for the purpose the apparatus which he had designed for the reduction of magnesium (p. 17), and adopting the readily fusible double chloride of aluminium and sodium as electrolyte. But, as the metal separated in pulverulent form at the low temperature of the fusion, he gradually added common salt to the mixture during the progress of the experiment until the temperature at last was raised almost to the melting point of silver. After cooling, the metal was found in large reguline spherical masses, which could be melted into a regulus by projecting them into fused common salt at a white heat.

Bunsen's account of these experiments was despatched to the Editor of *Poggendorff's Annalen* on July 9, 1854; and only a few weeks later, on August 14 of the same year, H. St. Claire-

* *Phil. Trans.*, 1808, pp. 1, 333.　　† *Phil. Trans.*, 1810, p. 16.
‡ *Pogg. Ann.*, 1854, vol. xcii.

Deville laid his thesis on metals, treating especially of aluminium, before the French Academy of Science.

Deville's Process.—As statements have crept into many text-books to the effect that Deville intentionally left Bunsen's process unnoticed, that portion of the thesis which has reference to his experiments* with Bunsen's magnesium apparatus, and which adduces his reasons for modifying the arrangement is here given in the form of a literal translation from the original French.†

"Up to the present time it has appeared to me impossible to obtain aluminium from aqueous solutions by means of the galvanic battery ; and I should even now believe in the absolute impossibility of doing so if the brilliant experiments of Bunsen, in the production of barium, chromium, and manganese, had not shaken my convictions. However, I am compelled to say that all the processes of this kind which have been published recently in reference to the preparation of aluminium have given me only negative results.

"Every one knows the beautiful process by means of which Bunsen has produced magnesium by decomposing magnesium chloride with the aid of the galvanic battery. The illustrious professor at Heidelberg has opened a way which may lead to results that will be interesting from many points of view. However, there can be no hope of applying the battery to the direct decomposition of aluminium chloride, which is a substance that does not fuse, but that volatilises at a low temperature ; it is necessary, therefore, to find a composition for the metallic bath that shall involve the use of a fusible material from which aluminium alone can be deposited by the electric current. I have found such a substance in the double chloride of aluminium and sodium, the production of which is a necessary feature of the extraction of aluminium by sodium. This chloride, which is fusible at about 185° C., and remains fixed at a sufficiently high temperature, although it is volatile at temperatures above the fusing point of aluminium, fulfils all the required conditions. I introduced this substance into a porcelain crucible, which was imperfectly separated into two compartments by a plate of biscuit porcelain, and decomposed it by means of a battery of five elements, using carbon electrodes, the crucible being heated, and the temperature being increased continually, in order that the charge might be maintained in the fluid condition as it became gradually less and less fusible ; but the fusing temperature of aluminium was not exceeded. Arrived at this point, I stopped the experiment, and, after lifting out the diaphragm and the electrodes, I heated the apparatus to a bright red heat, and found at the bottom of the crucible a regulus of aluminium, which was

* *Ann. de Chimie et de Phys.*, 1854, vol. xliii., p. 27.
† [This translation is taken from Deville's original paper.—Translator.]

rolled and was exhibited to the Academy at its meeting on March 20, 1854. It was accompanied by a considerable quantity of carbon, which had prevented a notable portion of the metal from uniting into a single mass. This carbon resulted from the disintegration of the very dense sample of retort carbon that served as electrode; and as a result of this action the positive electrode was entirely eaten away in spite of its thickness, which was very considerable. This disposition of apparatus (as used by Bunsen for magnesium) was not convenient in the case of aluminium; and the process to which I have been led, after many experiments, is as follows:—The aluminium bath is prepared by weighing 2 parts of aluminium-chloride and adding to it 1 part of marine salt in the state of dry powder. The whole is mixed in a porcelain crucible heated to about 200° C. Combination shortly sets in with evolution of heat, and there results a very fluid mixture, which is the bath used for the decomposition.
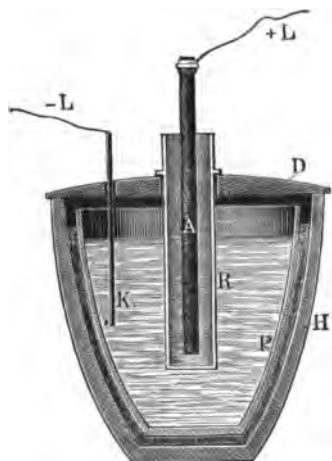
Fig. 59.—Deville's apparatus for reducing aluminium.

"The apparatus [Fig. 59] consists of a glazed porcelain crucible (P) which, as a measure of precaution, is placed within a somewhat larger fireclay crucible (H); the whole is surmounted by a crucible cover (D) pierced with a slot (L) through which is passed a wide and stout sheet of platinum (K) to serve as negative electrode, and with an aperture in which is tightly fixed a well-dried porous cell (R). Within the latter is placed a rod of retort carbon (A) as positive electrode. The bottom of the porous cell should be kept at the distance of some centimetres from that of the porcelain crucible. The porcelain crucible and the porous cell are filled to the same level with the fused aluminium sodium chloride, and the apparatus is heated after the manner described. The electrodes are then introduced and the current is passed through the apparatus. Aluminium is deposited with some sodium-chloride upon the platinum plate, and chlorine together with some aluminium-chloride is disengaged in the porous cell: fumes are thus produced which are destroyed by introducing dry and powdered marine salt at intervals into the porous cell. This salt is transported to the negative pole during the operation, along with the aluminium. A small number of elements (two are actually sufficient) are required to

decompose the chloride, which presents only a feeble resistance to the electric current.

"The platinum plate is raised from time to time, as it becomes sufficiently charged with metallic and saline deposit. It is allowed to cool, the mass of salt is rapidly broken, and the plate is replaced in the circuit. The crude material detached from the electrode is fused in a porcelain crucible enclosed within a fire-clay crucible. After cooling, the mass is treated with water, which dissolves a large quantity of sodium-chloride; and a grey metallic powder is left, which is re-united into a regulus by several successive fusions, adding double chloride of aluminium and sodium, if necessary, during each fusion."

Although the process of Bunsen and Deville for extracting aluminium could not have been carried into effect on a commercial basis, owing to many difficulties that stood in the way, their work must be said to have laid the foundation of our present methods — viz., the electrolysis of fused aluminium compounds.

Practical Obstacles to the Electrolysis of the Chlorides. —Deville's researches proved that the use of carbon cathodes was not perfectly adapted to aluminium reduction. Experience has shown that carbon rods or crucibles, when employed as cathodes, appear almost to melt, so great is the disintegration produced by the metal separated in their pores. An insurmountable obstacle to the practical use of this plant is found in the chemical action of the electrolyte and deposited metal upon every material of which the apparatus might be constructed; and no suitable substance has yet been found for the manufacture of melting and electrolysing-vessels, which are to be heated externally, and used with the haloid salts of aluminium. Both the fused salt and the metal itself absorb so many impurities in this way, during the electrolysis, that the valuable properties of the reduced aluminium are destroyed. The ordinary fireclay and plumbago crucibles contain silicates which become reduced by contact with the separated metal, and the latter is thus contaminated with silicon. With this property is associated that of very slight resistance to the action of melted haloid compounds (excluding the fluorides). Porcelain vessels not only have the faults of the above crucibles, but are very fragile and costly, whilst they are only to be had in small sizes. Crucibles of compressed carbon are so porous, that they cannot be heated externally when filled with a liquid substance, unless they are protected by an outer coating of an impermeable material. Finally, there are no metals, which could be practically applied, that are sufficiently refractory, and that are yet neither liable to attack by the electrolyte, nor capable of alloying with aluminium.

The production of pure aluminium by these methods, there-

fore, has failed, owing to the want of suitable materials for the, melting vessel and the cathode.

The Teaching of Deville's and Bunsen's Experiments.—Deville, in the treatise to which reference has been made, brought forward a suggestion that has hitherto almost escaped notice, but that deserves to be better known than it appears to have been, by reason of the important principle that it enunciates. He there describes the conditions under which metallic objects, especially those made of copper, may be coated with aluminium by means of his process. In this case, in order to maintain a constant proportion of aluminium in the fused aluminium-sodium-chloride bath, he recommends *the use of anodes of aluminium or of a compressed mixture of alumina and carbon.*[*] He thus described two most noteworthy principles, which have been repeatedly re-discovered and patented, viz. : —

1. *The use of soluble anodes in fused electrolytes ;* and

2. *The addition of aluminium to fused compounds of the same during electrolysis, by the agency of alumina.*

The first patent which contained the same idea was taken out in England under the name of Le Chatelier.[†] In this case it is probable, however, that the patent was applied for with Deville's full knowledge, because Deville frequently refers in laudatory terms to Le Chatelier as his collaborator. But, in addition to the use of alumina-carbon anodes, this patent also covers *the use of a porous cell for the reception of the anodes,* which tend to disintegrate during the electrolysis and so to introduce impurities into the electrolyte. It is, however, needless to point out that porous cells could not possibly be employed in the melted haloid salts of aluminium for the manufacture of that metal. But since the use of alumina-carbon anodes is accompanied by a tendency to disruption and hence by the introduction of impurities into the bath, and since the bath itself has a very low electrical conductivity, it is evident that Deville's invention cannot be applied in this form. At the same time, the fact that the practical application of Bunsen's and Deville's processes is not directly possible must not be allowed for a moment to detract from the service which these investigators have done in preparing the way for the modern, developments of their ideas. It is necessary to understand the reasons why experiments have failed in order to attain to success. The work of Bunsen and Deville formed the basis upon which has rested the success obtained in this field within the last few years, as may be shown by the following deductions, that may be drawn from the results (both positive and negative) of their work, in reference to the properties of the raw materials, final products, and substance used in the construction of the required apparatus :—

* H. St. Claire-Deville, *De l'Aluminium* (1859), p. 95.
† English Patent 1214, 1861.

1. *Aluminium may be obtained by the electrolysis of fused* (*anhydrous*) *aluminium compounds.*

2. *The aluminium separated from the fused material may be replaced by the use of alumina,* so that the process may be made more continuous.

3. The addition of aluminium to the electrolyte is *not to be effected* practically with the aid of *anodes composed of alumina and carbon,* although

4. The use of *soluble anodes* for the electrolytic refining of metals is of great importance.

5. *Cathodes made of carbon cannot be employed* (p. 121).

6. There is *no material* known, that is suitable *for melting vessels* to be used for the electrolysis of aluminium compounds *when external heating is applied.*

This, then, was the condition of affairs at about the middle of the present century. The last obstacles were removed, almost thirty years later, by the solution of the difficulties mentioned under the fifth and sixth heads. Before passing to the methods at present in use, it will be advisable to mention separately some of the proposals and experiments which, to judge at least from their original descriptions, could not possibly lead to the desired result.

Impracticable Processes.—First among these is Gaudin's process,* by which a melted mixture of cryolite and common salt was to be decomposed by the current into aluminium and fluorine. That of Kagenbusch† scarcely requires criticism : clay, melted with suitable fluxes, was to be electrolysed with the addition of zinc ; and the zinc was afterwards to be removed from the alloy by distillation or by a refining process. The process specified in Berthaut's patent‡ is practically identical with that invented by Deville. Faure's apparatus (1880) for the decomposition of aluminium chloride may also be passed over without comment.

Graetzel's patent § describes a process that is well known but quite impracticable. It is, however, referred to in many chemical text-books as being not only sound in principle, but as being in actual operation. It must, therefore, be examined somewhat more carefully than would be otherwise necessary. The inventor proposes to electrolyse melted chlorides or fluorides in the apparatus shown in Fig. 60. The melting vessel, *s,* is made of porcelain, stoneware, or similar fire-resisting material. and is protected from the direct action of the flame by a metal jacket. Within the inner vessel is a cathode of metal, preferably of aluminium ; whilst the anode is a carbon rod, K, enclosed in a porcelain tube, G, provided with openings, *g,* below and an

* *Moniteur Scientifique,* vol. xi., p. 62. (See Richard's *Aluminium,* 1890.)
† English Patent 4811, 1872. (See Richard's *Aluminium,* 1890.)
‡ English Patent 4087, 1879. § German Patent 29,962.

escape pipe, *p*, for chlorine, above.   During electrolysis, a current of reducing gas is circulated through the fusion chamber, B, by means of the tubes, o^1 and o^2.   In order to reduce the electromotive force required, as well as to maintain the strength of the bath, which would otherwise become impoverished, there are introduced into the inner vessel, G, besides the anode, but quite independent of it, plates or rods, M, which are composed of equivalent weights of alumina and carbon.   The carbon is to combine with the oxygen of the oxide whilst the metal of the latter passes into combination in the bath.   Unfortunately, the carbon does not give the desired result, but only serves to introduce impurities into the electrolyte.   In order to obtain the aluminium pure, it must be separated in the molten condition ; but in that case it may well be asked what would become of the aluminium cathode, the clay melting vessel, or, if these survived, of the separated aluminium itself ?   The introduction of reducing gases is at the least superfluous in the electrolytic deposition of aluminium.   After the foregoing remarks, there is but little of the invention left for criticism.   Lest, however, it should be said that those who were tempted to repeat the experiments with this apparatus, were so unskilful that they failed to recognise its advantages, it should be added, as an especially significant fact, that Graetzel himself, in his capacity as manager of the *Hemelinger Aluminium- und Magnesium Fabrik*, did not use his own process for obtaining aluminium, but that of Beketoff (see p. 103), which consisted in the reduction of cryolite by means of magnesium.   He applied for a patent for his process in various countries, but the application was refused, to the best of the author's knowledge, everywhere excepting in England.

The process brought forward by Anthony Zdziarski,* although not practically workable in the manner described, has yet some interest in connection with certain later patents.   Cryolite, or other aluminium compound, is mixed with suitable fluxes, and melted in a wrought-iron or plumbago crucible, heated in any convenient furnace.   At the bottom of the crucible is placed a metal which

Fig. 60.—Graetzel's aluminium electrolysing-vessel.

* English Patent 3090, Feb. 11, 1884.

is to be alloyed with aluminium ; and, during electrolysis, this metal forms the cathode, while the anode is a carbon rod dipping into the fused bath. The fluxes actually forming the electrolyte must contain substances which can readily combine with the fluorine separated at the anode, whilst they should also be as rich as possible in aluminium. Mixtures answering to these requirements may be obtained by fusing cryolite or other aluminium compounds with carbonate of soda or potash, or with other carbonates behaving in a similar way in respect to fluorine. After some general remarks upon the expenditure and the action of the current, and the injuriousness of silica when present in the metal mixture, it is further remarked :—"When a mixture of an oxide of aluminium (Al_2O_3) is employed, the flux must be used in a quantity sufficient to give an easily fusible combination. In this case the flux should consist of carbonate of potash, or soda, or both." The ideas expressed in this patent specification undoubtedly contain more matter for consideration than do those of most other inventions, which are, for practical reasons, unworkable.

Farmer * proposes (as an alternative amongst other aluminium compounds) *to melt* and electrolyse even *aluminium chloride in open vessels*. The melting-vessel is to serve also as cathode ; and the patentee thus revives in the year 1885 an idea which had been well known so long ago as 1808.

Grousilliers,† in searching for a patent, has not forgotten that aluminium chloride is easily vaporised under ordinary conditions, and therefore proposes to accomplish the electrolysis of this salt in closed vessels under pressure—a method of work which is obviously impracticable.

At first sight (but only thus) Grabau's patent specification ‡ would appear, by the use of cooled electrode cells, to afford a means of preventing that absorption of impurities by aluminium, which is so troublesome when fused salts are electrolysed. In explaining his process, Grabau gives the following example :—In the electrolysis of a fused bath of cryolite and sodium chloride it is known that chlorine is evolved at the positive pole, and aluminium in the liquid condition at the negative. But since melted cryolite is capable of attacking every known fire-resisting and non-conducting material, this electrolytic process can only be applied when, as is rendered possible in the present process, the affected parts of the apparatus are protected from the action of the fused salts or the separated constituents of the bath, by the use of an insulating and resisting shield. In Fig. 61 is shown an arrangement suitable for use in the process under description. The iron melting vessel, A, is heated by external

* U.S.A. Patent 315,266.
† German Patent 34,407. [English Patent 8478, July 14, 1885.]
‡ German Patent 45,012.

firing until the bath is thoroughly fluid; and the level of the latter should then be at X X.   The hollow metallic cylinder, B, is made with double walls, through which, for cooling purposes, a fluid such as water or air may be circulated, r being the inlet and r^1 the outlet pipe.   Another double-walled vessel, in the shape of a trough, C, is employed as a reservoir for the reception of the melted aluminium which separates.   The liquid or gas to be used in cooling this vessel enters the space between the walls by r^2 and leaves it by r^3.   In consequence of the cooling action produced by this circulation, a portion of the melted salt solidifies over the whole of the cooled surface of the cell, B, of the collecting vessel, C, and of the tubes, and forms at
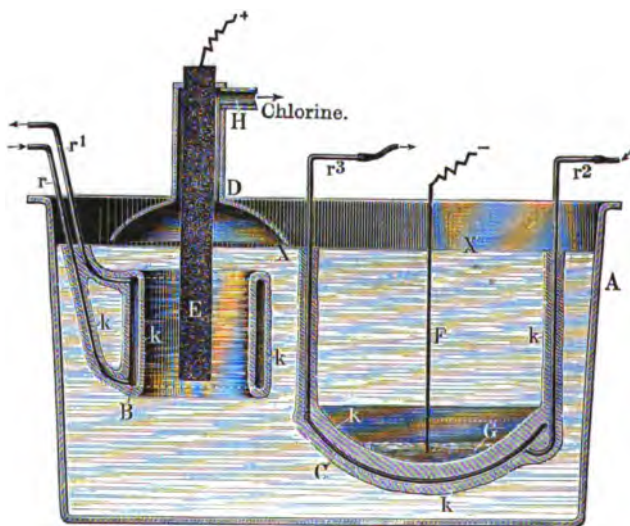
Fig. 61.—Grabau's cooled cell apparatus.

these places a non-conducting crust, which is not capable of being attacked either by the fused salts or by aluminium.

Grabau proceeds from the assumption that only those parts of an electrolyte vessel containing fused cryolite, which come in contact with the separated elements, can lead to the introduction of impurities into the bath and the metal.   If this were true, he would certainly almost have afforded a solution to the difficult problem of extracting pure aluminium electrolytically.   He can only be said in that case to have *almost* solved the question, because he does not state in his specification the nature of the cathode, with which the separated particles of aluminium will have to come into the most intimate contact.   Further, it appears to be doubtful whether, by the use of the anode cell as

it is shown in Fig. 61, the chlorine would be efficiently removed. The author's experience is that a large proportion of the chlorine which rises from the anode, tends to float on the surface of the fused salt, and to approach the walls of the vessel, and there, by contact with iron, to introduce impurities into the bath, and hence into the resulting aluminium. But putting these imperfections aside, the author has never succeeded in electrolysing mixtures of aluminium salts or double salts, containing fluorine, in iron vessels without both the bath and the metal taking up much iron. The want of durability of iron vessels when used
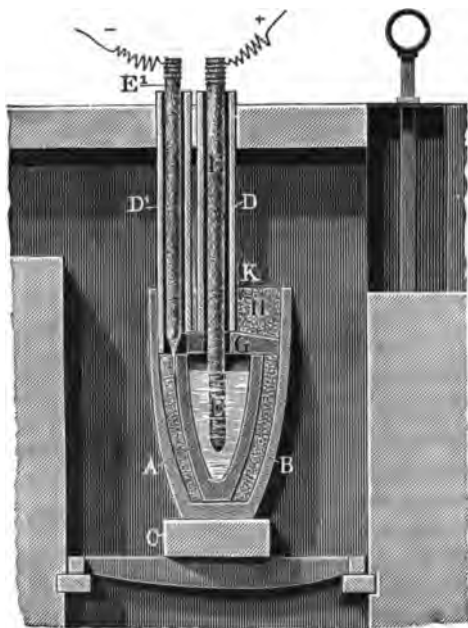
Fig. 62.—Henderson's apparatus (aluminium).

for these processes is in itself both a proof of this assertion and a ground of objection to such processes.

Henderson[*] approaches very closely to the modern process in his patent, according to which he electrolyses a solution of alumina in melted cryolite, and renews the alumina which is decomposed during the progress of the reduction. But he shows by the description of his apparatus that he has not recognised the principal faults of the older systems, for he uses as his cathode a carbon crucible heated externally. Fig. 62

[*] English Patent 7426, 1886.

shows the carbon crucible, A, serving as cathode, and protected
externally by the plumbago crucible, B, the space between the
two being filled with powdered graphite.   The connection with
the negative electric cable is effected by the carbon rod, E^1,
enclosed within a clay tube, D^1, whilst the carbon anode, E, also
surrounded by a clay tube, D, projects through the cover, G, of
the crucible, A, and there makes electrical connection with the
positive lead.   The lid, G, is covered first with a layer of
alumina, H, and then with one of clay.   The whole arrangement
stands on a fireclay slab, C, and is thus supported in the furnace,
by the heat of which the charge of cryolite and alumina in the
crucible is melted.   A current of 3 volts should suffice for the
separation of the aluminium from the alumina, which is con-
stantly replaced as it becomes decomposed.

Lossier[*] alone has, up to the present time, patented the
electrolytic separation of pure aluminium from aluminium
silicates.

Richards[†] describes an unpatented process of Rogers,[‡] which
aims at electrolysing melted cryolite with a cathode of molten
lead.   Here an alloy of lead and sodium is used initially, and
this separates aluminium at the expense of the sodium.   The
American Aluminium Company, of Milwaukee, which was
founded in 1887 to apply this process, appears, however, to have
contented itself with the erection of a small experimental plant.

A. Winkler,[§] of Görlitz, has not stated the nature of the
material of which his electrolysis-vessels were made, but as the
phosphates and borates of alumina were used as electrolytes, he
must have met with even less success than did his numerous
predecessors.   The separation of pure aluminium from a bath
of fused borates—even from aluminium borate itself—could
scarcely be proposed seriously by anyone who has ever seen an
account of Wöhler's work with boron.

Patents granted to Feldmann recommend the use as electrolyte
first of mixtures of the double fluoride of aluminium and barium,
strontium, calcium, magnesium, or zinc, with a chloride of one
of the latter metals[||]; and afterwards of the haloid salts of
aluminium with the oxides of more electro-positive metals.[¶]
The latter process has also been patented by Cowles.[**]

Daniel [††] has proposed an unlikely apparatus for the electro-
lysis of fused aluminium-sodium chloride; and even combines
it with a plant for the production of aluminium chloride by
Wöhler's method.

* German Patent 31,089.   † Richards' *Aluminium*, 4th Ed., 1890.
‡ *Proceedings of the Wisconsin Natural History Society*, April, 1889.
§ German Patent 45,824.
|| German Patent 49,915, 1887.   [[English Patent 12,575, Sept. 16, 1887.]
¶ German Patent 50,370, 1889.   ** English Patent 11,601, 1890.
†† German Patent 50,054, 1889.   [English Patent 4169, Mar. 9, 1889.]

Diehl * patents the electrolysis of the fluoride, Al_2F_6 . NaF, prepared by a special method, using sodium chloride in the fusion and a carbon electrode. Having recognised the uselessness of such cathodes (p. 121) he substitutes for them, at a later date, others consisting of ferro-aluminium (Al_3Fe), which are to take up aluminium during electrolysis until they contain the equivalent of Al_2Fe. He works with a current density of 13 to 20 amperes per sq. in. The excess of aluminium contained in the richer alloy is removed by heating, and the residual Al_3Fe is again used as cathode.

Other inventions, the details of which were either previously known or are impracticable, have been made more recently by Berg,† Dixon,‡ Graetzel,§ Diehl,|| Faure,¶ Case,** Gooch and Waldo,†† and others.

Successful Reduction Processes.—Some ten years ago attempts were made to produce the heat necessary for the fusion of the aluminium compounds, which were to be electrolysed, by the conversion of electrical energy within the melting vessel itself; and, in this way, the key to the successful solution of the problem has been found. The production of heat by the agency of electricity was attempted in two ways: either by introducing the electric arc into the melting chamber or the mass to be heated, or by including the electrolyte as a resistance in the electric circuit. Only the latter way has proved economically successful; but some attention may be devoted in the first case to those processes and arrangements which have for their object the decomposition of aluminium compounds in the zone of the electric arc.

Decomposition of Aluminium Compounds by the Electric Arc.—The electric arc serves even too well for the purpose of aluminium extraction. Although the two required conditions of heating and electrolysis are here available, yet the temperature is unnecessarily high for the end sought, even when a small arc is employed; and, moreover, this excess of heat is concentrated within a very small area. The use of the electric arc for the extraction of aluminium must, therefore, be considered extravagant.

The impulse to use this source of heat is traceable to the publication by Sir W. Siemens of an account of his electric smelting furnace, of which a description will be given after reference has been made to some of the earlier experiments and proposals.

* German Patent 59,406, 59,447; and English Patent 813, Jan. 16, 1889.
† German Patent 56,913, 1889. [cf. English Patent 2002, Feb. 6, 1890.]
‡ English Patent 16,794, Oct. 24, 1889.
§ German Patent 58,600, 1890. || German Patent 62,353, 1891.
¶ German Patent 62,907, 1892.
** U.S.A Patents 512,801, 512,803, 1894.
†† U.S.A. Patents 527,846, 527,851, 528,365, 1895. [English Patent 20,615, Oct. 17, 1894.]

The temperature obtainable in the electric arc seems to have been first utilised in experiments made by Depretz. In a note to the French Academy of Science, of December 17, 1849,[*] he describes the behaviour of a small retort of sugar charcoal (of about $\frac{9}{16}$ in. diameter) within which the arc was formed with the aid of a carbon point. The retort itself served as positive electrode.

Johnson's Process.—A somewhat later invention for the smelting of ores was patented by J. H. Johnson[†] in England on March 22, 1853. The ore was mixed with carbon and placed in the electric arc, which was caused to play between two large electrodes; the ore thus became fused and converted into metal and slag. These two substances fell into a receptacle placed to receive them, where, by means of a suitable furnace, they were kept in the fluid condition until the metal had separated from the slag (compare Gerard-Lescuyer, p. 135). The same specification contained also a description of a somewhat different apparatus.
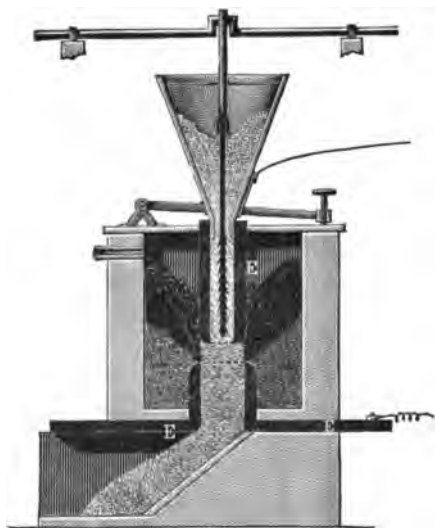
Fig. 63.—Cowles' ore-smelting furnace.

The two electrodes were arranged so as to include an angle between them. The upper was hollow and was filled with the ore to be reduced, which was to be gradually impelled forwards by a screw. In connection with this description it is interesting to examine a sketch (Fig. 63) which is taken from an English patent specification of H. Cowles.[‡] In this figure, E E are the electrodes, into the upper of which the ore is fed by means of a funnel, and so passes to the neighbourhood of the arc, while the fused products pass out beneath.

It is not impossible that the Johnson named in the above patent was only the agent for the real inventor, for the first part of the above description would suit an apparatus which was described by Pichou in the year 1853, and is considered by

* *Comptes Rendus*, 1849, vol. xxix.   † English Patent 700, 1853.
‡ English Patent 4664, 1887.

Andreoli* to be the first electric smelting furnace; this apparatus is shown in Fig. 64, which is reproduced from the original sketch. Here, O O are carbon rods gripped by the holders, A A, X X are the conducting wires, T T are screws to advance the carbons into the furnace, M is masonry, N is the smelting hearth with a grate placed beneath it, and L is the chimney. In the then state of
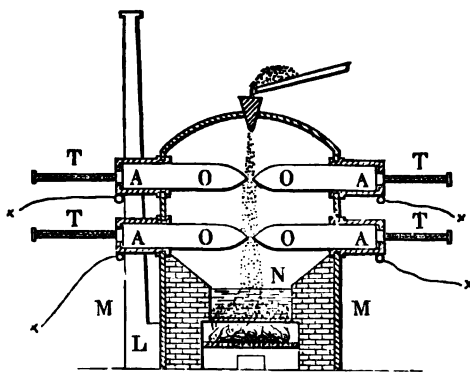
Fig. 64.—Pichon's smelting furnace.

technology the practical use of this invention was out of the question; but the possibility of applying it was never lost sight of.

The Siemens Electric Furnace.—Sir William Siemens' electric furnace† for refractory materials showed in principle little that was new. It was not proposed to use it for the extraction of aluminium. The whole arrangement of the details of the furnace, however, forms so interesting an object of comparison with the productions of the modern inventor, shortly to be described, that a description of the apparatus must not be omitted here.

Siemens himself has described ‡ the apparatus. A crucible, T (Fig. 65), made of graphite or other very refractory material is placed in a metallic case, H, the space between the two vessels being filled with powdered charcoal or other bad conductor of heat. A rod of iron or platinum, or of gas-carbon, such as is used for electric light purposes, is passed through a hole in the bottom of the crucible. The cover of the crucible is also bored in order that the negative electrode may be passed through it. For this electrode is used, if possible, a cylinder of compressed carbon, which should be of uniform measurement; it is suspended from the end, A, of a beam, A B, supported in the centre

* *Industries*, 1893.   † English Patent 2110, 1879.
          ‡ *Elektrotechnische Zeitschrift*, 1880.

by means of a strip of copper or other good conducting material, whilst to the other end, B, of the beam, a hollow cylinder of soft iron is so fastened that it can move freely in a vertical plane within a coil of wire, S, which offers a total resistance of about 50 ohms.   The magnetic force by which the hollow iron cylinder is drawn into the solenoid-coil, is balanced by a counterpoise, G, which may be moved freely along the beam, A B.   The resistance of the arc is determined, and, within the limits imposed by the source of power is fixed, by the shifting of the sliding weight to any required point.   The one end of the solenoid-coil is connected to the positive, the other to the negative, pole of the electric arc.   Hence an increased resistance of
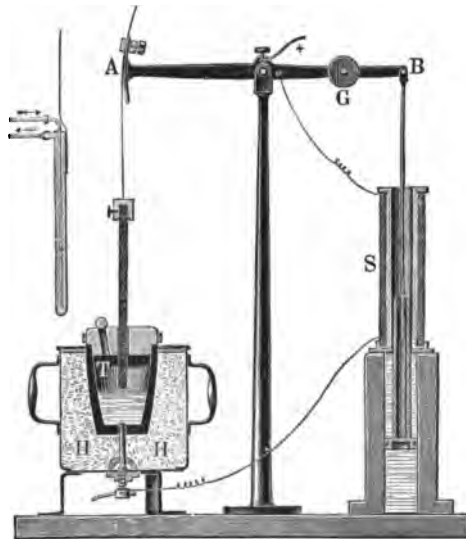
Fig. 65.—Siemens' electric furnace.

the arc leads the negative electrode to sink to a greater depth within the crucible, whilst a diminished resistance causes the counterpoise to press the iron cylinder deeper in the coil, whereby the length of the arc is increased until equilibrium is restored between the opposing forces.   This automatic regulation is of the highest importance, for without it the temperature in the crucible would, on the one hand, diminish, while, on the other hand, the sudden diminution in the electric resistance of the materials during the melting would produce not only a sudden increase in the resistance of the arc, but probably also the extinction of the latter.   It is essential to the satisfactory performance of electric fusion, that the substance to

be melted should form the positive pole of the arc, because, as is well known, heat is generated at this pole. This arrangement is evidently suited for use with metals only, for non-conducting earths or gases it is necessary to provide an indestructible positive pole which is also capable of being melted, and so of forming a layer of liquid at the bottom of the crucible. The heat accumulates very rapidly. With the aid of a medium sized (36 "Webers" *) dynamo a crucible 8 in. deep, set in non-conducting material may be brought to a white heat in less than a quarter of an hour, and 2 lbs. of steel may be melted in it within half an hour from the commencement. To check the consumption of the negative pole, the author [Siemens] uses a water-cooled electrode, or a tube of copper through which a stream of cold water is made to circulate. This consists of a simple copper cylinder, closed at the lower end, and containing a caoutchouc tube
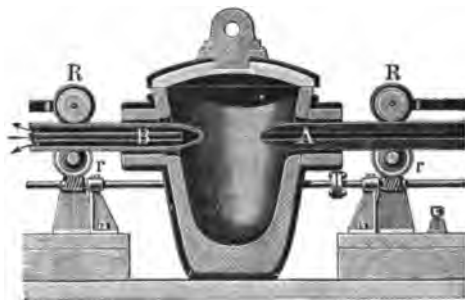
Fig. 66.—Siemens' modified electric furnace.

which reaches nearly to the bottom and serves to convey into it a stream of water.

The adjoining sketch (Fig. 66) is taken from the English patent specification.† Of the electrodes, A is made of carbon, whilst B is a metal tube cooled by cold air or by water, as in Fig. 65. Each electrode is guided by a pair of rollers, R, r.

A common crucible steel furnace uses from 2½ to 3 tons of the best coke per ton of steel melted, a regenerative crucible furnace only 1 ton, and a regenerative gas furnace when used in connection with an open hearth, only about 12 cwts. The electric furnace therefore approximates to the regenerative gas furnace in respect of fuel economy. But the former has the following advantages :—1. The temperature attainable is theoretically unlimited. 2. The charge is melted in a completely neutral atmosphere. 3. The process can be conducted without much preliminary preparation, and under the direct supervision of the experimenter.

* [The Weber was the old electrical unit of quantity ; in the above place it may be translated amperes.—TRANSLATOR.]
† English Patent 4208, 1878.

4. Even when using the ordinary refractory materials, the limit of temperature that may be practically reached is very high, because in the electric furnace the substance which is being heated is hotter than the crucible, whilst in ordinary melting processes the temperature of the crucible must exceed that of its charge.   Although the electric furnace may not supplant the ordinary furnace, yet chemical reactions of the most varied kind may be in future carried on with its aid, and at temperatures hitherto unattainable.   In course of practical trials with this apparatus, it was found that 20 lbs. of steel could be completely melted in an hour, and 9 lbs. of platinum in a quarter of an hour, whilst copper which had been packed in carbon dust lost more than 90 per cent. of its weight by volatilisation.

Fig. 67.
Menges' electric furnace.
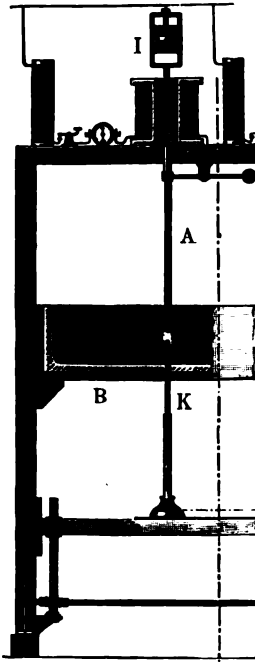
Fig. 68.

Fig. 69.
The Kleiner-Fiertz aluminium furnace.
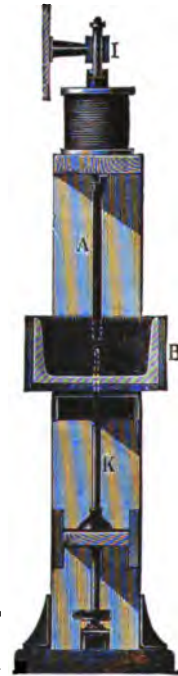
The Menges Electric Furnace.—The construction of Menges' * furnace shows but little novelty.   It may be pictured as an arc lamp with a fixed electrode at the bottom, attached to a crucible made of some conducting material, whilst the upper

* German Patent 40,354, 1886.

electrode, passing through the crucible cover, is kept suspended at the proper distance above the former, with the help of suitable mechanism. The movable electrode is made of a compressed mixture of a convenient electric conductor, such as carbon, with the metallic oxide that is to be reduced. The whole apparatus may be suspended within a closed jacket, in order that the fusion may be effected under pressure if desired. Fig. 67 shows the method of suspension, and the valves, manometer, and binding screws attached to the jacket.

The Kleiner-Fiertz Electric Furnace.—Kleiner-Fiertz * proposes to melt and decompose the double fluorides of aluminium in the electric arc. The electrodes of the apparatus (Figs. 68, 69) dip into a vessel, B, lined with clay and filled with cryolite and bauxite. The negative electrode, K, is capable of adjustment in a vertical plane, and the position of the positive pole is controlled by a weighted lever and a solenoid, its movements being limited and checked by a piston, I, plunging into a liquid, and placed above. It is difficult to say what advantage this arrangement has over that of Siemens. The practical success of the method, no doubt, remains far behind that anticipated for it by the inventors ; but it is not possible to imagine continuous work with any material, which, although comparatively easy to melt, has ample opportunity for re-solidifying owing to the concentration of the heat of the arc at so small a point in immediate proximity to cold material. An interruption of the current would be much more frequently necessitated by the freezing of the electrode into the charge, than by the decomposition of a sufficient quantity of the double fluoride in the bath.

The Grabau Electric Furnace. — Grabau's process and apparatus for melting or reduction by means of the electric arc† have not removed the difficulties described in connection with the Kleiner-Fiertz plant; indeed, they have the appearance of exhibiting these disadvantages in an even higher degree. The material to be melted is introduced beneath the surface of the fused mass in the crucible by means of tubes, and this mass forms one pole for the passage of the current. Various modifications are illustrated in the patent specification which allow the material under reduction to be added continuously, either alone, or associated with the metal that is to be alloyed with it. The alloying-metal at the same time is made to conduct the current. The fused mass is kept at a constant height by means of an overflow notch. The illustration and detailed description of this apparatus need not be given here for the reasons already indicated.

The Gerard-Lescuyer Furnace.—The apparatus (Fig. 70)

* German Patent 42,022, 1886. [Compare English Patents 8531, June 29, 1886, and 15,322, Nov. 24, 1886.]
† German Patent 44,511, 1886.

of Gerard-Lescuyer* affords a very good illustration of the furnace patented by Johnson in 1853. Instead of mixing the ore with carbon before submitting it to the action of the arc,
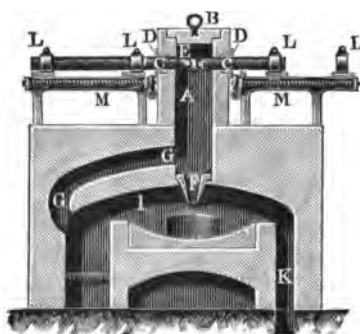
Fig. 70.—The Gerard-Lescuyer electric furnace.

he moulds it into bars with the aid of pressure, and in admixture with copper, alumina, carbon, and tar, and then uses these as electrodes for the production of the arc. In other respects the process is sufficiently described by Johnson's specification (p. 130).

The Electric Construction Corporation Furnace. —The furnace of the Electrical Construction Corporation† accomplishes the heating of the charge by means of the arc, as well as by resistances interposed between the electrodes; and the charge itself, if sufficiently conductant, may evidently constitute this resistance. In the vertical section, shown in Fig. 71, F is the shaft of the furnace, and a a hopper for the introduction of the charge. The hopper is closed with two sliding valves, A A, to exclude the air at the time of charging, and has a worm, B, to convey the material from a into the furnace. The electrodes, c' c', project from two opposite sides into the hearth of the furnace; they consist of carbon cylinders contained in metallic cases, c c, which are connected to the poles of the dynamo by the wires, d d. The cases, c (or the electrodes themselves, if they be of metal), can be provided with an arrangement for internal cooling by means

Fig. 71.—The Electric Construction Corporation furnace.

of water. The thin carbon or metal rods, c'', serve to start

* German Patent 48,040, 1887.   † German Patent 55,700, 1890.

the furnace by completing the electric circuit. They may be introduced through separate perforations in the walls of the furnace, and be in electrical connection with the cases, c, or they may be passed through central channels in the ordinary electrodes, c'; in the latter case, either one subsidiary electrode may be used which makes contact with the thicker pole (c') opposite, or two may be employed, one within each of the larger cylinders, c'. Any gases or vapours that may be evolved escape through the opening, g, in the upper part of the furnace, and slag is tapped off through h. The working doors, x, may be closed either by fireclay doors, or by a lute of the same material. In order to equalise the heat produced, the hearth of the furnace may contain either molten metal or any material that is a sufficiently good conductor. In charging, the space between the electrodes may be filled with fragments of coke, which then become heated to redness. Carbon powder may be strewn over the ends of the electrodes from the doors, x, to compensate for that which is lost by combustion.
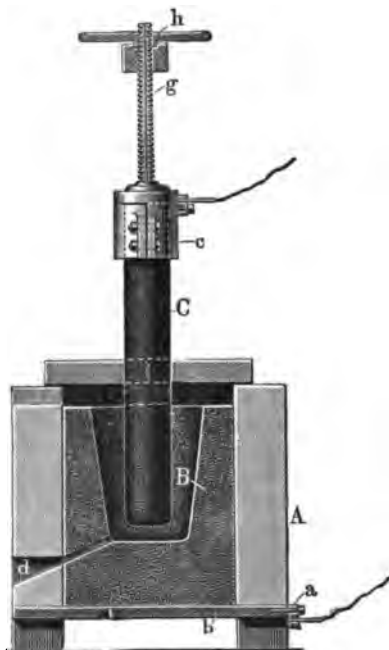
The Willson Furnace.—References to Willson's * process of

Fig. 72.—The Willson furnace.

producing aluminium are frequently to be found in technical literature. But, by the light of his patent specifications, aluminium could scarcely be reduced profitably, because, like Kleiner-Fiertz and others, he employs the electric arc for heating and electrolysis, which is both costly and extravagant. His first furnace was, at least, so far unlike that of Siemens' that he had introduced an arrangement by which reducing gases (or carbon powder and the like) might be injected into the arc,† in order

* U.S.A. Patents 430,453, June 17, 1890; 492,377, Feb. 21, 1893. English Patents 4757, March 17, 1891; 21,696, Nov. 28, 1892; 21,701, Nov. 28, 1892.
† [English Patent 9361, June 17, 1890.]

to assist the electrolytic action to some extent; but it is less easy to discover the points of novelty exhibited by his latest apparatus. A carbon crucible, B (Fig. 72), is set in masonry, A, and is connected by the metal plate, *b*, to *a*, which is joined up to the electric lead. A carbon rod, C, forms the other pole, and is joined by the holder, *c*, to a threaded spindle, *g*, by which vertical movements may be imparted to it with the aid of the hand-wheel, *h*. The material to be reduced is mixed with so much carbon that it cannot actually fuse ; yet the inventor expects the resulting metal to liquate from this excess of carbon, so that it may from time to time be withdrawn through the tap-hole, *d*, and he hopes that such a method will be practically successful.

The Electrolysis of fused Aluminium Compounds by Currents of very high Density for the Production of a Melting Temperature by the Heating Action of the Current.—It is perfectly well known that the electric current generates heat in passing through any conductor; and from Joule's Law, to which allusion was made in the introduction, it is further evident that the conversion of electrical energy into heat varies with the square of the current strength. The low conductance of the liquid conductors known as electrolytes, in contrast with that of simple conductors, necessitates the use of a very strong current for the former, especially if the electrodes be not immersed to any great depth ; and this current is indeed so powerful, that even refractory substances may be fused and brought into the liquid condition by the heat generated. In this manner the whole mass of the electrolyte becomes very uniformly heated during electrolysis; and this is a great advantage as compared with the localisation of the heat when the arc is employed.

The Héroult Process.—The introduction of this principle not only rendered the extraction of aluminium possible as a manufacturing process, but solved the difficulty, hitherto insuperable, of finding a suitable material for the construction of the melting vessels. At the present moment, all aluminium works make use of baths, which are kept fluid by electrical agency ; but the first and almost the only inventor who, so far, has given in his patent a good specification of this method of working, accompanied by clear illustrations, is the French chemist, Paul Héroult. In his [German] specification * he describes his invention as a "process for the production of aluminium alloys by the heating and electrolytic action of an electric current on the oxide of aluminium, Al_2O_3, and the metal with which the aluminium shall be alloyed." [The title of the

* French Patent 170,003, April 15, 1887; Belgian Patent 77,100, April 16, 1887 ; English Patent 7,426, May 21, 1887 ; German Patent 47,165, Dec. 8, 1887 ; U.S.A. Patent 387,876, Aug. 14, 1888.

English patent, which was taken out in the name of Henderson, is somewhat different, and covers a larger field; it runs thus— "An improved Process for the Preparation of Aluminium, Aluminium Bronze, and Alloys of Aluminium by Electrolysis."]

The method of heating will be sufficiently explained by the following description and sketch of an apparatus which was
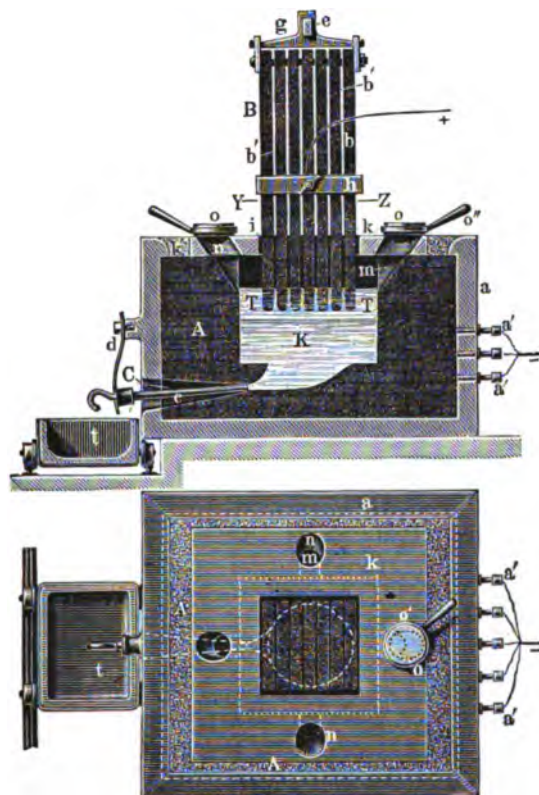
Figs. 73 and 74.—The Héroult aluminium furnace in longitudinal section, and in plan.

actually brought into use by the Swiss Metallurgical Company, now the Aluminium-Industrie-Aktiengesellschaft, at Neuhausen, in Switzerland. Fig. 73 shows a case of iron or other metal, *a*, insulated below and open at the top, and provided with a thick lining of carbon plates, A, which are held together by some carbonaceous cementing-medium, such as tar, treacle, or glucose. The material of which the case, *a*, is made must also be a good

conductor; and in order to ensure the most intimate contact between the outer surfaces of the carbon lining, A, and the inner side of the case, a, and hence to obtain a high conductance, the case may, with advantage, be made by casting it as a shell around the lining; the cooling of the mass will then produce the desired effect. Attached to a are a number of copper pins, a', which conduct the current, with the least possible electrical resistance, from the negative leads to the basin or crucible, A. In the crucible are immersed the ends of the positive electrode, B, the carbon rods composing which are either laid close together or are separated by small spaces, that must be filled up with a conductor, such as copper or carbon. At the upper ends, the carbon plates are held together by the frame, g, which is suspended from a chain by means of the eye, e, so that the whole electrode, B, may be brought into place, or raised or lowered at will. The lower frame, h, attached to the electrode, B, is provided with the necessary clamps or screws for making connection with the positive lead from the dynamo. With the exception of the space, i, around the electrode, B, and necessary for its free vertical movement, the melting chamber is closed entirely by the graphite plate, k, which, however, has openings, n, for the introduction of materials to the furnace. Channels are cut in the lining, A, to correspond with the apertures, n, and these channels, m, n, provide also for the escape of gases generated in the furnace. The movable plates, o, provided with the rim, o', and the handle, o", serve to cover the openings, n, during the progress of the melting process. The space between the graphite plate, k, and the rim of the case, a, is filled in with charcoal powder, as shown at k'.

In starting the operation, copper, preferably in a finely divided condition, is placed within the crucible, A; the sheaf of anode carbons, B, is lowered until it comes in contact with the copper, the current then traverses the latter and causes it to fuse. As soon as the bath of fluid copper, which forms the negative pole, is ready, alumina is introduced into the crucible, and the anode sheaf, B, is raised a little higher. The current now passes through the alumina, which melts and becomes decomposed, the oxygen uniting with the carbon, b, and burning it to carbonic oxide, which escapes as a gas from the mouth of the crucible, and the aluminium separated from its combination with oxygen being absorbed by the copper and forming aluminium-bronze. The crucible is now supplied with both copper and alumina, either continuously or intermittently, at a rate depending upon the progress of the electrolysis.

The anode sheaf, as already explained, must be raised or lowered according to the resistance in the circuit. This regulation may be made automatic by connecting the chain carrying the anodes, B, with a reversible electric motor, which is regulated

by the ampere meter and acts as an electric regulator. To tap off the melted aluminium-bronze which accumulates in the crucible, the mould, t, lined with carbon, is wheeled into position under the tap-hole, C; the carbon rod, c, is then withdrawn from the latter, and is only replaced when the mould is full. The electrolytic process is continued by lowering the carbon, B, deeper into the crucible again, and continuing the additions of copper and alumina as before. A current of about 13,000 amperes and 12 to 15 volts is to be recommended as suitable for this process.
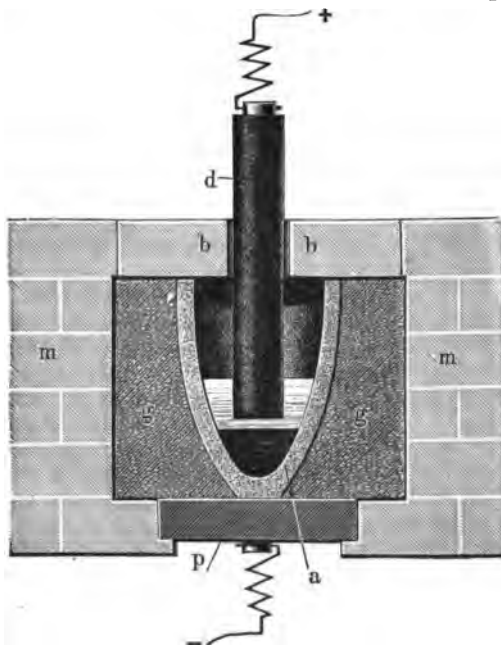
Fig. 75.—Héroult's aluminium-furnace for small installations.

So far the description has referred to the German patent specification. Those of other countries do not differ sensibly from the above, excepting that the sketch accompanying them shows a simpler form of apparatus,* which may be here reproduced (Fig. 75) since it is well adapted for use in smaller experiments, and also possesses some historic interest. The crucible, a, stands on a plate, p, of conducting material. The space between the crucible and the masonry, m, is filled with

* [The current values recommended in the English patent for a furnace of this type, with a crucible 8 in. (20 cm.) deep, internally, and 5½ in. (14 cm.) wide at the top, and with an electrode 2 in. (5 cm.) in diameter, are 400 amperes × 20 to 25 volts.—TRANSLATOR.]

powdered carbon, *g*. The carbon anode, *d*, passes through the cover, *b*, and the crucible itself forms the cathode.

According to the claims in the [German] patent specification this process is concerned in the production of aluminium alloys, and primarily with aluminium-bronze. Two obstacles stand specially in the way of its application to the extraction of pure aluminium—viz., first, the high fusing point of the alumina, and, secondly, the material of which the cathode is made. Deville himself pointed out that with a carbon cathode the process could not possibly work smoothly. The following pages will show how these difficulties have been obviated.

The Hall Process.—Recent publications relating to aluminium state that the metal is extracted in America under the Hall patents, and in Europe under those of Héroult and Minet. This statement stands in direct opposition to the author's criticism on the Hall and Minet processes in the first edition of the present work, which was to the effect that "*the American patents of C. M. Hall, as well as A. Minet's process, are founded partly on facts which have long been known, and partly on others which have been found to be inapplicable in practice.*"

If Hall or Minet have worked out processes which differ from those described in their patents, the author does not dispute the statement that certain factories may have one of these systems in operation.* But at this point the question under discussion is whether the process is worked according to the original Hall and Minet *specifications* which the author *still* holds *to be impracticable*. In the first place, the inventors may be allowed to speak for themselves in the actual words of their patent specifications, which are here given, together with reproductions of the original drawings.

The first application of Ch. M. Hall † was received in the Patent Office of the United States of America on July 9, 1886; it was divided, and formed the basis of the two patents 400,766 and 400,664 of April 2, 1889 (the day that the patent was granted).

Hall's American Patent, No. 400,766.—"The invention described herein relates to the reduction of aluminium from its oxide by dissolving such oxide in a bath containing a fused fluoride salt of aluminium, and then reducing the aluminium by passing an electric current through the bath, *substantially as*

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* [It may be noted in passing that the American Courts upheld the validity of Hall's patents, on the ground that the method of heating—externally by ordinary fuel, or internally by the current—is not an essential point, and that the patents covered the use of alumina dissolved in fused cryolite. The trial lasted for a long time, and judgment was given after the hearing of much evidence concerning prior processes. Both these processes are now in use, the Hall process at Niagara (see p. 149), and the Héroult in the South of France.—TRANSLATOR.]

† [Compare English Patent 5669, April 2, 1889.]

hereinafter more fully described and claimed. In the accompanying drawings, Fig. 76 represents a sectional elevation of a form of apparatus applicable in the practice of my invention, and Fig. 77 is a view partly in elevation and partly in section of a modified form of apparatus.

"In the practice of my invention I prepare a bath for the solution of the aluminium by fusing together in a suitable crucible, A, the fluoride of aluminium and the fluoride of a metal more electro-positive than aluminium—as, for example, the fluoride of sodium, potassium, &c.—these salts being preferably mingled together in the proportions of 84 parts of sodium fluoride and 169 parts of aluminium fluoride, represented by the formula, $Na_2Al_2F_8$. A convenient method of forming the bath consists in adding to the mineral cryolite $\frac{338}{421}$ of its weight of aluminium fluoride. The object of thus adding aluminium fluoride is to secure in the bath the proper relative proportions of the fluorides of aluminium and sodium. To the fused bath is added alumina, or the oxide of aluminium, in sufficient quantities, and the alumina being dissolved by the fused bath an electric current is passed through the solution by means of suitable electrodes, C and D, connected with a dynamo-electric machine or other
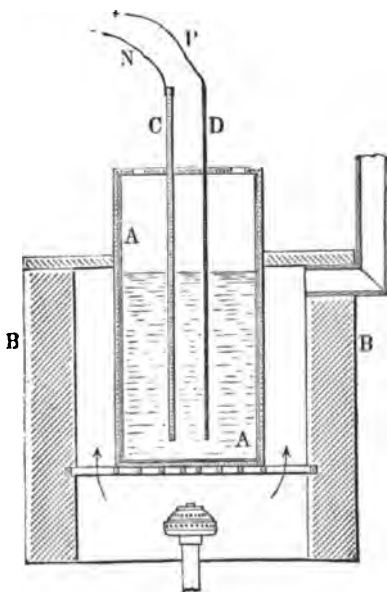
Fig. 76.—The Hall furnace, U.S.A. Patent, No. 400,766.

suitable source of electricity, and immersed in the solution. By the action of the electric current, which preferably has an electromotive force of about 4 to 6 volts, oxygen is released at the positive electrode, C, and aluminium is released at the negative electrode, D, which, on account of the affinity of aluminium for other metals, is *formed of carbon (!) when it is desired to produce pure aluminium.* The positive electrode may be formed of carbon, *copper, platinum,* or other *suitable* material. When formed of carbon the electrode, C, is gradually consumed, and must therefore be renewed from time to time; but when formed of copper an oxide coating is formed over the surface of

the electrode. This coating serves to protect the electrode from further destruction by the action of the oxygen, but does not interfere materially with the conducting qualities of the electrode.

"On account of the affinity of the aluminium for other metals, and also the corrosive action of the materials, I prefer to form the crucible, or melting pot, A, of metal—as iron or steel—and protect the same from the action of the aluminium by a carbon lining, A'. *This crucible is placed in a suitable furnace,* B, and subjected to a sufficient heat to fuse the materials placed therein, such materials fusing at approximately the same temperature as common salt.

"In lieu of the electrode, D (Fig. 76), the carbon lining, A', may be employed as the negative electrode, as shown in Fig. 77, the conductor from the negative pole of the electric generator being suitably (!) connected, as shown at N, to such lining.
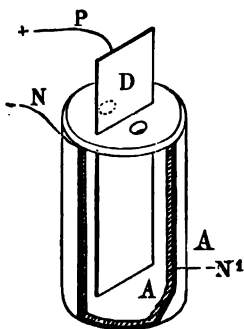
Fig. 77.

Modified apparatus, Hall patent 480,766.

"In order to render the bath or solvent more fusible, fluoride of lithium may be substituted for a portion of the fluoride of sodium ; as, for example, for one-fourth the fluoride of sodium, an equivalent amount of lithium fluoride by molecular weights may be substituted. Thus 26 parts of lithium fluoride displacing 42 parts of sodium fluoride, the resulting combination contains 26 parts of lithium fluoride for every 126 parts of sodium fluoride and 338 parts of aluminium fluoride.

"While I consider the proportions of fluorides of sodium and aluminium, and of the fluorides of sodium, lithium, and aluminium hereinbefore stated, are best adapted for the purpose, such proportions may be varied within certain limits without materially affecting the operation or function of the bath, as, in fact, any proportions which may be found suitable may be employed. The aluminium, as it is reduced at the negative electrode, is melted and collects thereon in globules, and then drops down to the bottom of the bath, which is of lower specific gravity than the molten aluminium, and can be removed by suitable means ; or the bath may be poured out, and after being cooled the aluminium can be picked out."

Clearly, in this patent, external firing is expressly prescribed for the heating of the crucible and its contents, and, further, the use of carbon cathodes is specified. These two claims make it quite evident that *the inventor at this time was still far from recognising the conditions that must be fulfilled in any process which is to be of practical use in the extraction of aluminium.*

Hall's American Patent, No. 400,664.—In this specification which agrees throughout with the preceding, both in idea and expression, another solvent for the alumina is first proposed :— "This combination which may be termed the 'double fluoride of aluminium and potassium' is preferably formed by mixing together 169 parts of aluminium fluoride and 116 parts of potassium fluoride, such proportions of the ingredients correspond-ing to the formula $K_2Al_2F_8$. A variation of these proportions within certain limits produces only immaterial changes in oper-ativeness of my process—as, for example (as I now believe the fact to be), a larger proportion of potassium fluoride increases the
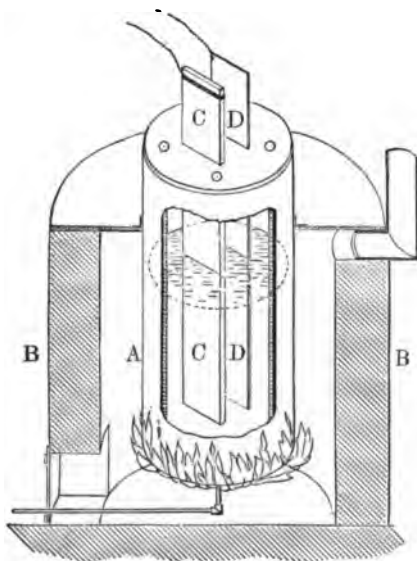
Fig. 78.   Fig. 79.   Fig. 80.
The Hall furnace, American Patent, No. 400,664.
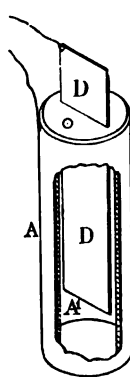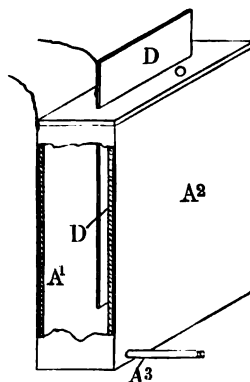
capacity of the bath for dissolving alumina, but at the same time lessens its fusibility, whereas a larger proportion of aluminium fluoride renders the bath more fusible but decreases its capacity for dissolving alumina.

"The combination of the fluorides of aluminium and potassium may be rendered more fusible and its capacity for dissolving alumina may be increased by the addition of lithium fluoride, or a partial substitution thereof for potassium fluoride—as, for example, the combinations of the fluorides of aluminium, potas-sium and lithium, represented by the formulæ $K Li Al_2 F_8$ or $K_3 Li_3 Al_4 F_{18}$, are effective as regards their capability for dissolving alumina, and are quite fusible."

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The apparatus, shown in the annexed Figs. 79, 80, 81, to be used in conducting the electrolysis is then described :—"The crucible, A, containing the above-described bath or solvent is *placed in a suitable furnace*, B, and heated sufficiently to melt the bath—*i.e.*, to approximately a low red heat. The electrodes, C and D, having suitable connections with a dynamo-electric machine, or other suitable source of electric energy, are then inserted into the bath and a sufficient amount of alumina placed therein. The alumina is dissolved by the bath, and by the action of the electric current aluminium is reduced at the negative electrode, D, and, being melted, sinks down to the bottom of the crucible."

There is a notable departure in this case from the practice described in the previous specification, inasmuch as *any material containing carbon* is here expressly *excluded* from use in preparing the *anodes*, and copper or platinum is recommended as a substitute. As in the last patent, the inventor holds it possible to use the carbon lining, A, of the crucible (Figs. 72 to 74) as cathode. In addition to iron or steel, copper is mentioned as a material suitable for the crucible. An electromotive force of 3 to 4 volts still suffices for the current.
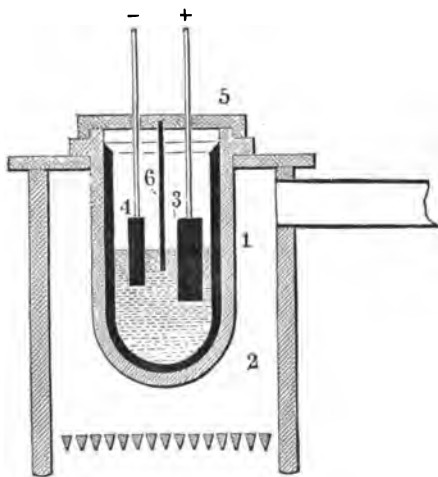
Fig. 81.—The Hall furnace, American Patent, No. 400,665.

Hall's American Patent, No. 400,665.— In this specification the use of the previously patented solvents or electrolytes is disclaimed as being unsuitable. A new recipe is given instead, and it is accompanied by the description of a new apparatus. The previously patented bath, formed of the double fluoride of aluminium and an alkaline metal, "becomes less efficient after being subjected to electrolytic action for some time. This change does not result from any removal of aluminium fluoride or of fluorine from the bath, as no fluorine is separated; but a black or dark substance is formed in the bath, apparently from the alkaline constituent of the same (!), which interferes with a free electrolytic action, and increases the electrical resistance; hence,

it has been found necessary, when employing the salts named, to change the bath after a continuous use of the same."

This difficulty is circumvented in the following way :—"A double fluoride of aluminium and calcium is used, having a composition represented by the formula $CaAl_2F_8$. This composition is formed by 169 parts of aluminium fluoride to 78 parts of calcium fluoride or fluor spar, the aluminium fluoride being artificially prepared by saturating hydrated alumina with hydrofluoric acid. The fluorides of calcium and aluminium unite in forming a double fluoride more fusible than the fluoride of calcium and, as I believe, more fusible than either constituent alone. While I prefer to use the double fluoride of calcium represented by the formula $CaAl_2F_8$ in carrying out my process, there are a large number of similar double fluorides of the same metals which may be used, and which closely resemble the one named, and answer almost, if not quite, as well as a bath for dissolving the alumina. Thus the double salt of the formula $Ca_3Al_2F_{12}$ has been successfully employed. . . . The fluorides above mentioned are placed in the carbon-lined crucible or vessel, 1, arranged in the furnace, 2, and subjected to sufficient heat to fuse the material. Electrodes, 3 and 4, *formed of carbon*, when pure aluminium is to be deposited, are connected to a suitable electric generator, as a dynamo-electric machine. If an alloy is desired, the negative electrode, 4, is formed of the metal with which it is desired to alloy the aluminium. Alumina in the form of bauxite (!), anhydrous oxide of aluminium, or any other suitable form of alumina, preferably the pure anhydrous oxide Al_2O_3 artificially prepared " . . . (The decomposition of the oxide is described as in other specifications.) . . . " The solution of alumina in the fused bath of the double fluoride of aluminium and calcium is apparently heavier than the metal aluminium, and hence this metal, if unalloyed, rises after being reduced and floats to the surface of the bath, where it is liable to loss by oxidation in contact with the air or with the positive electrode, where it is subjected to a strong oxidising action; hence when reducing aluminium the crucible, 1, is provided with a cover, 5, provided with openings for insertion of the electric conductors and the escape of gas from the crucible, and with a partition, 6, of carbon extending down into the bath and from side to side of the crucible, and separating the two electrodes."

Neglecting the electrolyte for a moment, it will be seen that this devious path has after all only led back to Bunsen's original apparatus.

Then, again, " As the operation continues, the cover is removed from time to time and the aluminium removed from the surface of the bath. . . . The specific gravity of the bath may be lowered by the addition to it of other salts lighter than the double fluoride of calcium and aluminium, so that the pure

aluminium will sink in the combination. . . . Thus, by the addition to the bath above described of about two-thirds its weight of the double fluoride of potassium and aluminium ($K_2Al_2F_8$), which is comparatively a very light salt, is formed a combination lighter than aluminium." Finally, in place of the calcium aluminium fluoride, the double fluoride of the other alkaline earth metals may be used. These salts of the alkaline earth metals are preferable to the alkaline double fluorides, because the operation of the current is in no way affected by their saturation with alumina.

Hall's American Patent, No. 400,666.—Here, again, a new bath is employed. It is true that good results had been obtained with the electrolytes previously named, but the black precipitate (see preceding specification) is undesirable. Hence "an electrolyte or bath is formed of the fluorides of calcium, sodium, and aluminium, the fluorides of calcium and sodium being obtained in the form of fluor spar and cryolite respectively, and the fluoride of aluminium being obtained by saturating hydrated alumina ($Al_2(OH)_6$) with hydrofluoric acid. The compound resulting from the mixture of the above-mentioned fluorides, which is re-
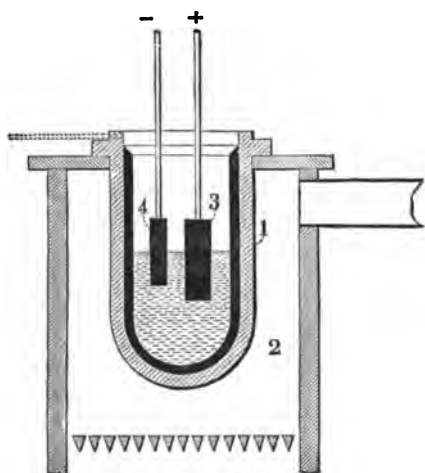
Fig. 82.—The Hall furnace, American Patent, No. 400,666.

presented approximately by the formula $Na_2Al_2F_8 + CaAl_2F_8$ is placed in a suitable vessel, 1, preferably formed of metal and lined with purpose of pure carbon, for the purpose of preventing the admixture of any foreign material with the bath or with the aluminium when reduced. *The vessel, 1, is placed in a furnace, 2,* and subjected to sufficient heat to fuse the materials placed therein. Two electrodes, 3 and 4, of any suitable material, preferably carbon, when pure aluminium is desired . . . are placed in the fused bath, or, if desired, the carbon-lined vessel may be employed as the negative electrode, as represented in dotted lines . . . The reduced aluminium sinks down to the bottom of the vessel, the bath being of a less specific gravity than the aluminium."

In other details this specification varies but little from those previously quoted, excepting that from 3 to 4 per cent. of calcium chloride is to be added to the bath. The electromotive force is now estimated at 6 volts.

Hall's American Patent, No. 400,667.—This final patent protects the following proposal:—A suitable bath consists of "fluoride of calcium, 234 parts; cryolite, the double fluoride ($Na_6Al_2F_{12}$), 421 parts; the fluoride of aluminium, 845 parts, by weight, and about 3 to 4 per cent. (more or less) of a suitable chloride—*e.g.*, calcium chloride. Alumina is then added to this bath, preferably in sufficient quantities to form a saturated solution. . . . Electrodes . . . are then inserted in the bath, the negative electrode being formed of carbon when pure aluminium is desired. The positive electrode may be formed of carbon or other suitable (!) material."

There are here, then, repeated the possibilities and impossibilities which have been described and patented previously, so that there is nothing new to be extracted from these specifications unless it be the somewhat altered composition of the bath and of the electromotive force required, which varies from 4 to 8 volts. These were the patents to which the criticisms in the previous edition of this book were applied, criticisms to which the author still adheres. A later patent (1893) granted to J. B. Hall will be referred to subsequently.

[Practical Installation of the Hall Process. — The Pittsburg Reduction Co. have put down a very large installation of the Hall plant at their Niagara
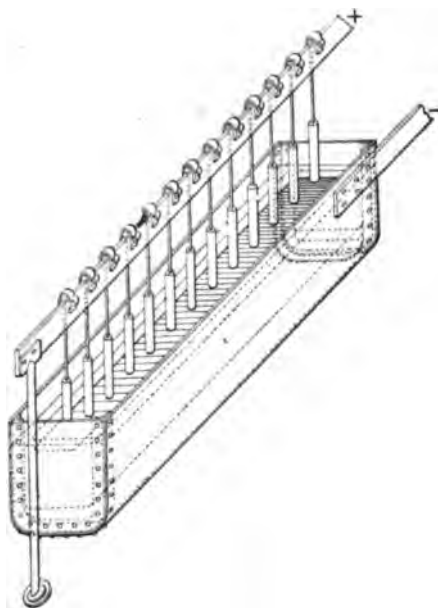
Fig. 82A.—The Pittsburg Co.'s Hall furnace.

works, where it is now in full operation. The following description, based on a paper read by Hunt [*] before the Institution of Civil Engineers, seems to indicate, however, that the details of

[*] *Journ. Inst. Civ. Eng.*, 1896, vol. cxxiv., p. 208.

the process have been to some extent modified since the publication of the specifications quoted above.

The electrolytic tanks (of which one is shown in Fig. 82A) consist of iron troughs lined with carbon, and are connected up in series. A stout copper bar is riveted to the outside of each trough, and serves to make electrical connection either with the anodes of the adjoining trough or with the negative conductor of the generator, according as the trough occupies an intermediate or (the negative) end position in the series. The tank itself, therefore, with any aluminium that it may contain, acts as the cathode. The anodes are carbon rods suspended from a copper bar, which is placed above the vat, and are partly immersed in the fused electrolyte; as these carbons are gradually consumed by the oxygen liberated in contact with them, they must be lowered from time to time into the bath. It is found in this installation that the weight of carbon thus burned is approximately equal to that of aluminium reduced. The carbon linings are not appreciably affected, and should (with the iron containing-pots) last for several months in continuous use.

The process depends on the electrolytic decomposition of alumina dissolved in the fused bath. The following rules for guidance in the selection of a solvent have been laid down by Hunt, and although they will for the most part be self-evident to those who have carefully read the present chapter, they may be quoted here :—

1. The solvent, with its charge of dissolved ore, must be fluid at a comparatively low temperature, in order to obtain the proper conductivity and to allow the reduced aluminium to sink in the bath.

2. The solvent must be able to dissolve, and to retain in solution, at least 20 per cent. of alumina at the working temperature.

3. The (thermo-chemical) heat of formation of the solvent must be such that the latter will not be more readily decomposed than the dissolved ore.*

4. The specific gravity of the solvent, when molten, must be less than that of fused aluminium, in order to prevent short-circuiting by metal floating to the top and forming a bridge between the electrodes, and to avoid the re-oxidation of aluminium at the surface.

5. There must be no solid (insoluble and infusible) bye-product to clog the pot and to prevent (electrical) continuity.

6. The molten solvent with its dissolved ore must be a good conductor of electricity.

7. The solvent must have no corroding action on nascent aluminium (i.e., on the metal at the moment of deposition).

* The electrical pressure theoretically required for the dissociation of alumina is 2·8 volts, whilst that for the fluorides of sodium, calcium, or aluminium is 4 volts or more.

The composition of the bath may evidently be varied very considerably without sacrificing any of these conditions; but the mixture most commonly employed is said to consist of 677 parts of aluminium fluoride, 251 of sodium fluoride, and 234 of calcium fluoride. In starting the process, the ingredients are either fused in separate vessels and transferred to the electrolyte tanks in the molten condition, or they are melted in the tanks themselves with the aid of the current. When the bath is thus prepared, pure alumina is added, and the supply should be constantly renewed as the metal is deposited, so that the electrolyte may always contain about 20 per cent. of the dissolved oxide. The temperature of the bath is kept below 982° C. The operation is continuous, and the aluminium is withdrawn from the bottom of the bath from time to time, as it accumulates, either by a siphon, or by means of a ladle, in which case care must be taken to withdraw as little as possible of the molten salts with the metal. It is necessary that both the alumina and the anode carbons should be as pure as possible, because all the foreign substances present in them will pass into the bath; and then, since aluminium is very electro-positive in character, they will for the most part enter into the reduced metal. The same care need not be taken in the preparation of the electrolyte, and the various salts used may be such as are commonly sold in commerce. The reason of this is that the impurities (such as silicon, lead, zinc, and copper) present in them are more electro-negative than aluminium, and are completely eliminated by deposition within the first two days of use. With care, the solvent should only require renewal at long intervals, so that after the first two days the only impurities that can be present in the aluminium are those derived from the carbon anode and lining, and from the added alumina.

No satisfactory information is given as to the cost of working, nor as to the actual current employed. It is simply stated that, theoretically, 0·7476 lb. of aluminium is the equivalent of 1000 ampere hours, and that the amount of energy required to reduce 1 lb. of the metal from alumina is about 5 H.P. hours. This, of course, is on the assumption that 746 ampere hours yields 0·554 lb. of aluminium (see last column of table on p. 9), and that the electrical pressure required for dissociation is 2·8 volts; so that a current of 746 amperes × 2·8 volts (i.e., of 746 × 2·8 watts, or of 2·8 E.H.P.) should yield 0·554 lb. Al per hour. In practice, the author says, this is "very nearly approached." It must, however, be remembered that the heating of the bath is effected by means of the electric current, which has thus to supply sufficient energy to raise the added alumina to the temperature of the bath, as well as to make good the loss of heat from the whole apparatus by conduction and radiation; and that there is resistance to be overcome in the circuit, which

also adds to the consumption of power. Even by allowing the utmost elasticity to the expression quoted in inverted commas, it would seem that considerable advance must have been made since Addenbrooke gave the yield obtained by the Hall process as 1 lb. Al per 22 E.H.P., and since Richards stated it to be 1 lb. per 16 E.H.P.

The only estimate of cost given is that attributable to Roberts-Austen, in which he stated the production of 1 lb. of aluminium to require as follows :—

For Energy, ...	1·1d.
„ Alumina, ...	6·0d.
„ Labour and superintendence, . . .	1·5d.
„ Interest, repairs, and maintenance, . .	2·0d.
„ Chemical stores, ...	1·0d.
„ Carbon electrodes, ...	2·0d.
	13·6d.

Owing to recent improvements, however, some reduction must be made in these figures, as, for example, in the second item, the yield of aluminium from alumina is nearly quantitatively correct, and therefore 1 lb. of deposited aluminium should demand the use of about 2 lbs. of added pure alumina, the market price of which in Germany is now less than 2d. per lb.

The magnitude of the industry, and the vast strides made by the British Company, which is at present the largest producer of aluminium in the world, may be gleaned from information published in January, 1897,* to the effect that the Pittsburg Co. are now using 1450 effective H.P., and the British Aluminium Co. are employing 2500 H.P. at their Falls of Foyers Works in Scotland.—TRANSLATOR.]

The Minet-Bernard Process.—Now, as to the Minet patent, which was subjected to similar criticism.   To prevent misunderstandings, which might arise from an incorrect comprehension of newspaper accounts, it may be stated that Minet's and Bernard's processes are identical.   Minet's process was first put into operation at the factory of the Brothers Bernard, and the patents are taken out in the names of these gentlemen.

The first application for a patent † was made in England in July, 1887, when provisional protection was sought; the complete specification with drawings was presented in that month, and was accepted on February 17, 1888.   The latter runs thus :—" Among the salts of aluminium, some are very slightly fusible, while others are volatile, and in order that an electrolytic action may be produced it is essential that the salt to be electrolysed should be in a particular state of liquefaction, which is very difficult to be obtained with aluminium salts.   Thus the

* *Industries and Iron,* 1897, vol. xxii., p. 21.
† English Patent 10,057, July 18, 1887.

chloride of aluminium is too volatile, while the fluoride of aluminium is not fusible enough.

"It has already been proposed, as regards the first, to combine it with the salt of another metal, and to thus form a double salt which imparts to it a little more fixity, and allows it to be subjected at a relatively low temperature to the action of the current in order to extract the aluminium therefrom. But the double salt thus formed—that is to say, the double chloride of aluminium and of sodium—is an exceedingly unstable body which is handled with difficulty, and it gives rise to extremely noxious vapours, hence it cannot be used commercially for the extraction of aluminium therefrom by electrolysis; in all cases great losses are occasioned.

" It has been sought to render it still more fluid by mixing it with small quantities of chloride of sodium, and even of cryolite (double fluoride of aluminium and of sodium); this latter body being then adopted solely as a flux. Now, experiment shows that if the current be passed through a bath composed of double chloride of aluminium and of sodium, chloride of sodium, double fluoride of aluminium and of sodium (cryolite), the double chloride is volatilised to a great extent, and the fluoride of aluminium, which is more fixed than the former, is decomposed by the current (?).

"A bath has, therefore, been formed, in which the fluoride of aluminium is contained in larger proportions, either in the form of a single salt or in the form of a double salt, *the fluoride not being employed, according to their invention, as a flux, but being used as the principal electrolyte*, which will be subjected to the action of the current. Experiment shows, moreover, that the yield in aluminium increases with the proportion of fluoride of aluminium contained in the bath. It reaches its maximum when the fluoride of aluminium is found in a melted state without being mixed with any other salt. Very good results are obtained with the following proportions:—Fluoride of aluminium = 40, chloride of sodium = 60 parts. A double salt of sodium and of aluminium, such as natural or artificial cryolite, may even be used, not as a flux, but as an electrolyte in the following proportions:—Cryolite = 20 to 50, chloride of sodium = 80 to 50 parts. It must be understood that there can be employed as electrolytes in the bath mixtures or compounds of fluorides of sodium and of aluminium in different proportions to those in which they are found in cryolite; for instance, fluoride of aluminium = 35, fluoride of sodium = 10, chloride of sodium (or other flux) = 55 parts.

"Electrodes.—Their nature may vary according to the state in which the aluminium metal is to be deposited, the following list comprises the most general cases. For pure aluminium, either carbon anodes and cathodes, or carbon anodes and copper

or iron (cast iron) cathodes; for aluminium bronze, red-copper or carbon anodes and copper or carbon cathodes; for ferro-aluminium, iron or carbon anodes and cathodes. In short, metal or graphite may be employed without distinction as electrodes.

"The crucible may be of refractory earth, of plumbago, or of metal (iron, cast-iron, red-copper, platinum, and the like), and in cases where an alloy is required the crucible itself may serve as the cathode, or as the anode.

"Besides platinum, which is unalterable but costly, the other metals are attacked by the bath (mixture of chloride of sodium and fluoride of sodium), and have still a further defect, that is to say, that, *when they are subjected to the direct action of the flame,*
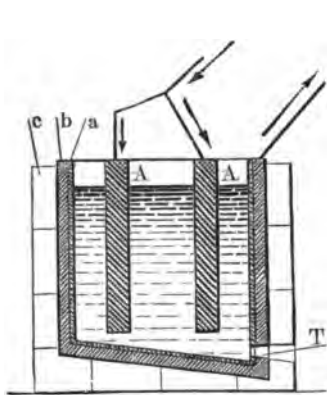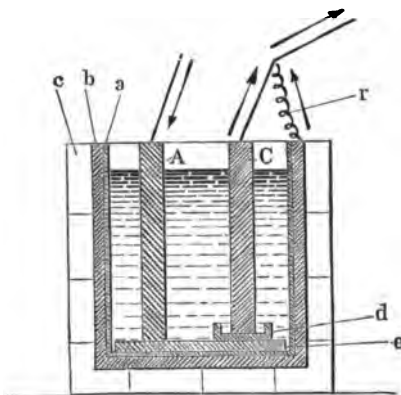
Fig. 83.　　　　　　　Fig. 84.

Bernard (Minet) aluminium furnace.

or to too high a temperature, they allow the bath to filter through, hence a considerable loss results.

"With the arangements hereinafter described, with reference to the accompanying drawings, such defects are obviated. Figs. 83 and 84 show a general view of the tanks arranged in such a manner that the bath cannot filter through. It is sufficient for this purpose to provide the metallic tank, *a b*, outwardly with a thin brick wall.* The bath is prevented from becoming dirty in consequence of the metal of the tank being attacked by means of two entirely different arrangements according as it is desired to obtain an alloy of aluminium, or pure aluminium alone.

"First arrangement, Fig. 83. For the formation of aluminium alloys. The tank is made of the metal which forms a component

* This wall is stated in the French specification as being used *to protect the vessel from the coke fire employed to bring it to a red heat.*

part of such alloys. A A are the carbon anodes; *a b* is the metallic tank serving as a cathode. At the beginning of the operation, and as fast as aluminium is produced by electrolysis, there is formed on the inner surface of the tank a layer, *a*, of the aluminium alloy to be obtained. When this alloy is sufficiently rich in aluminium, the metal formed anew electrolytically runs to the bottom of the tank. As shown in Fig. 83, the bottom of the said tank is slightly inclined, and is provided with a tap-hole, T, which allows after a lapse of time, determined by means of experiments, the withdrawal of the fused aluminium containing smaller or greater portions of the metal forming the tank, which is not a defect, as the object to be attained was the formation of an alloy.

"Second arrangement, Fig. 84. For the formation of pure aluminium. Let A be the anode or anodes, and C be the cathode or cathodes. The cathode, C, is arranged in a small crucible, *d*, placed upon a plate, *e*, these two apparatus being formed of fused alumina, or fluoride of calcium, or of carbon blocks. *a b* is the metallic tank arranged in derivation with the cathode. The resistance, *r*, interposed between the cathode and the metal tank is sufficiently great so that the derived current in the tank represents only a small portion of the whole current (5 to 10 per cent.). It serves to form upon the inner surface of the tank an alloy of aluminium, and of the metal forming the said tank, which alloy protects the latter, and is only feebly acted upon by the bath. The metal which is deposited in the crucible, *d*, in this arrangement is nearly pure.

"Having now particularly described and ascertained the nature of my said invention, and in what manner the same is to be performed, I declare that what I claim is :

"The hereinbefore described process for the extraction upon a large scale of aluminium by electrolysis, and comprising the extraction of pure or alloyed aluminium, the characteristic features of said process being :

"1. The electrolysis of a metal bath where fluoride of aluminium (in the state of a single or a double salt) is used, not as a flux, but as the main electrolyte, being subjected to the influence of the current.

"2. The use of a brick covering for the metallic tank so as to avoid the filtration of the bath.

"3. The use of the tank as a cathode for the production of an alloy of aluminium, or at least of aluminium destined to form an alloy with the metal constituting the tank.

"4. The use of a derived current on the tank when it is required to obtain pure aluminium.

"5. The use of fused alumina and of fluoride of calcium (or carbon blocks) for the formation of plates, and of the crucible serving for the production of pure aluminium."

The above specification offers no suggestion whatever that the bath is to be heated electrically, although this forms the very foundation upon which the successful extraction of aluminium is based. On the contrary, it is much more clearly explained that the crucible is to be protected *externally by masonry against the action of flame*. The old error of using carbon cathodes is still adhered to. The feeding of the bath during electrolysis by the use of aluminium compounds, such as alumina, was not thought of at the time that the patent was taken out. The criticisms above alluded to apply therefore with full weight, not only to the Hall, but to the Minet patents also.[*]

It must be specially remarked as noteworthy in the Hall patents that an endeavour is made to find a solvent for aluminium that shall be fusible at a low temperature. The fifth claim in the Bernard-Minet patent would have been of some weight had not the drawing (Fig. 84) shown that the inventor had no idea of the only right use for the material of which he proposed to construct his crucible. A crucible made of alumina or fluor spar after the fashion of *d*, in Fig. 84, would have become dissolved by the melted bath in a very short time.

Fig. 85.—Aluminium reduction. Apparatus used at Neuhausen.

The Neuhausen-Froges Process.—In the year 1890 a very carefully written, illustrated description of an apparatus that was in use at the aluminium works then existing (Neuhausen and Froges) went the round of the technical journals.[†] Fig. 85 shows the arrangement in question; it consisted of an iron crucible, lined with charcoal, and resting on an insulating stand, through

*[It has been stated by Chénevau in the *Revue de Physique et de Chimie* (vol. i., p. 55), that, in applying the Minet process at St. Michel, Savoy, 30 per cent. of cryolite mixed with 70 per cent. of sodium chloride is used as a charge, bauxite and aluminium fluoride being introduced during electrolysis. The electrical pressure required is 7·5 volts for each bath, and the out-turn is equivalent to 0·88 oz. of aluminium per horse-power hour.—TRANSLATOR.]

† *Industries*, 1890, vol. viii., p. 499.

the bottom of which was passed a metallic negative pole.
The positive pole, made usually of a carbon rod built up of
separate plates united together, was suspended in the crucible
from above. A solution of alumina in melted cryolite was used
as electrolyte, and this was brought up to the necessary fusion
temperature by the great evolution of heat in the bath caused by
the employment of a very high current density. At first the
metal pole inserted in the bottom of the crucible, and afterwards
the melted aluminium which was deposited upon it, served as
cathode. The crucible was charged originally with cryolite, and
later with alumina; and then more alumina was added as required
to take the place of that which had been decomposed by the
current. The aluminium collecting at the bottom of the crucible
was run off from time to time, whilst the oxygen of the alumina
united with the carbon of the anode to form carbonic oxide and
carbonic acid.

Borchers' Aluminium Extraction Apparatus.—The author has
vainly endeavoured to produce pure aluminium in an apparatus
of corresponding construction to that just described. He is
unwilling to condemn an apparatus, or process, which other
metallurgists have held to work satisfactorily, merely because *his
own* experiments with it have given negative results; yet he
has been unable to avoid the suspicion that the anonymous
writer of this article had not been accurately instructed con-
cerning all the details of the plant, for he (the author) had
obtained the most satisfactory results under otherwise similar
circumstances with an apparatus which he had constructed for
various experimental purposes. This apparatus is shown in
Fig. 86, in which it has been intentionally presented in a form
externally resembling, as far as possible, that of the apparatus
figured in the preceding illustration. In all probability the
internal arrangements of the two are also practically the same.

An iron crucible, T, with a fireclay bottom, B, is lined
internally (F) with alumina or other difficultly fusible aluminium
compound. The steel plate, K, is let into the lining of the
bottom, and into it is screwed the copper tube, R, which may
be cooled by means of water or other suitable medium. A
narrow side tube, E, introduces the water for cooling, whilst the
inner tube, X, reaching nearly to the top of R, serves as an
escape pipe. The tube, R, and, through it, the steel plate, K,
which acts as cathode at the beginning of the experiment, are
put in connection with the main conducting cable, N, by means
of the clamp, V. The carbon rod, A, forms the anode; it is
supported by an iron clamp, attached to a threaded-iron rod, which
in turn is screwed into the iron base plate, U; and the current
is conveyed to the arrangement through the copper rod, P,
which makes a ring-connection with the iron supporting rod.
The metal accumulating at the bottom of the crucible during

the operation is run off at intervals through the tap-hole, S, into the mould, G, whilst the gases evolved at the anode escape through the openings in the cover, D, which also serve for the admission of the charge of alumina. The crucible, T, is insulated from P by a fireclay (chamotte) plate, I. The lining, F, in spite of its solubility in the bath, is sufficiently protected by the cooling action of the air playing around the walls of the crucible.
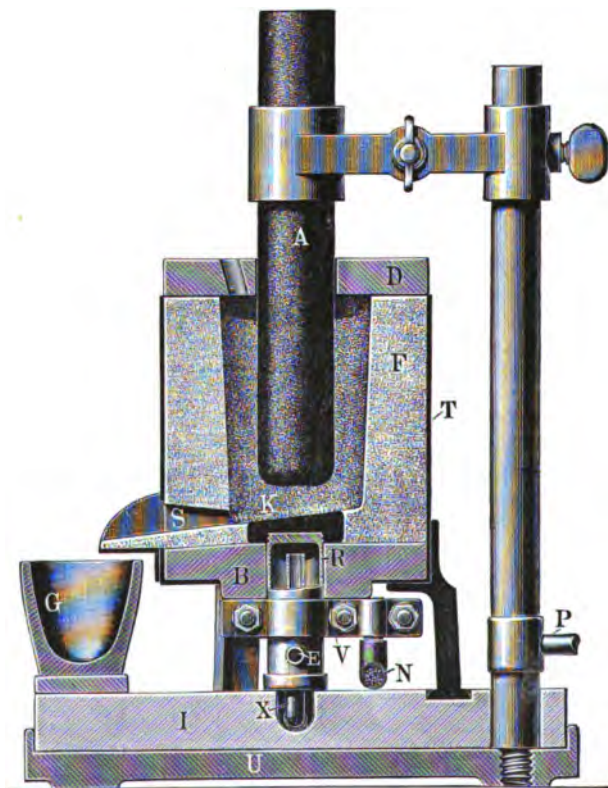
Fig. 86.—Borchers' aluminium extraction apparatus.

For operations of long duration, and with a high current density, further protection may be afforded by introducing cooling arrangements into the lining.

An apparatus adapted to research purposes has been constructed by the author, to be operated by a current of 120 to 200 amperes and requiring an electromotive force of from 5 to 12 volts, according to the current density required and to the nature of the electrolyte.

The working of this apparatus is very simple. The tap-hole is first closed with a clay or oxide stopper, and a little aluminium (or metal to be alloyed with the aluminium) is placed on the bottom of the crucible. The anode is now caused to approach the cathode; and if the former be shaped to a point, it will become rapidly and highly heated as soon as it comes in contact with the metal resting upon the latter; but if it be shaped according to the illustration (Fig. 86), it is advisable to introduce a thin carbon pencil between the electrodes, and then, as before, the necessary melting temperature will be quickly attained. A small quantity of the mixture to be smelted (oxide and salts, or sulphide and salts) may be placed in the crucible initially with the aluminium, if desired; the remainder of the mixture (or the whole, as the case may be) must now be gradually introduced through the opening in the cover. It will then be found that as soon as the charge has melted, and the electrodes have become separated by a layer of fused electrolyte, the contents of the crucible will remain fluid, and electrolysis will commence. In order to replace the electrolyte, as it becomes decomposed, alumina is similarly added throughout, mixed at first with a considerable proportion, but later with smaller quantities, of the salt that is employed as solvent. The separated metal may be removed through the tap-hole after the lapse of sufficient time, or at the end of the experiment.

The absorption of impurities is quite prevented by a sufficient cooling of the cathode, but the cooling must not of course be pushed to excess. The crucible itself stands freely exposed on all sides, so that, in most cases, the natural cooling of the surrounding air will suffice to maintain intact the oxide lining, F, in the crucible, T. The separated metal, therefore, comes in contact at the sides with its own oxide only, and at the bottom with the material forming the cathode, which it is unable to dissolve so long as the water supply is properly maintained within R.

The Kiliani Aluminium Extraction Apparatus.—The following apparatus was constructed and used (probably, as the author thinks, before his own) by Kiliani,* who was formerly manager of the *Aluminium-Industrie-Aktien-Gesellschaft;* but the patent specification only describes the mechanism employed in imparting motion to the anode, making no reference to the lining of the vessel or to the disposition of the metal pole which serves as cathode. The details of the drawing suggest that the crucible may have been arranged for use after the manner of that employed by the author. The publication of any account of the practical installation of this furnace in respect of lining, cathodes, and the like, is not to be looked for, because manufacturers can

* German Patent 50,508, April 21, 1889. [English Patent 6745, April 20, 1889.]

hardly be expected to give to the world the secret processes and practical details which they have adopted as the result of patient and laborious experiment.   Hence the following account is derived only from the description given in the patent specification.   The columns, *a*, support the vessel, *b*, which is intended for the fusion of the electrolyte; the cathode enters this vessel below, and makes connection with the negative pole of the generator by the conductor, *c*.   The cross piece, *d*, carries the arrangement for giving support and motion to the positive electrode, *e*. Within the sleeve, d^1, is the anode spindle, *f*, which in vertical section has the form of a rack, so that it may engage with the pinion, *g*, the latter being actuated by the worm and wheel, $h\ h^1$, in connection with the handwheel, h^2.   The teeth and notches in the spindle, *f*, take the form of rings and grooves respectively, which are cut round the whole of its circumference, so that if turned upon its axis it may in any position act as a rack and thus be still in gear with the pinion, *g*. A worm wheel, *k*, is so keyed on to the spindle, *f*, that the latter is free to move in the direction of the bore of the wheel.   The wheel, *k*, gears into the worm, *i*, which is mounted on the axis of a driving pulley.   Electrical connection with the anode is effected by means of branches in the boring of the spindle, *f*.   When this mechanism is in action, the anode will be maintained in constant rotation by means of the worm wheel, while vertical motion may be imparted to it in either direction by the hand wheel, h^2.
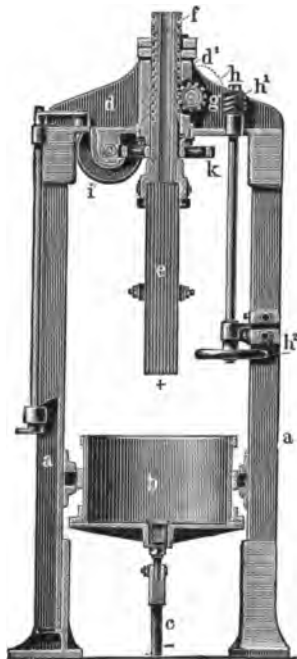
Fig. 87.—Kiliani's electrode mechanism.

The Grabau Patent.—Some more recent patents have introduced into the field both new solvents for alumina and new electrolytes.   Grabau * recommends a melted mixture of aluminium fluoride or oxy-fluoride with alkaline carbonates, and recovers an alkaline fluoride or cryolite as a bye-product, according to the equations :—

* German Patent 62,851, 1891. [English Patent 10,090, June 13, 1891.]

$$2Al_2F_6 + 6Na_2CO_3 + \underset{(Anode)}{3C} = \underset{(-)}{4Al} + 12NaF + \underset{(+)}{9CO_2}$$

$$4Al_2F_6 + 6Na_2CO_3 + \underset{(Anode)}{3C} = \underset{(-)}{4Al} + 2(Al_2F_6.6NaF) + \underset{(+)}{9CO_2}$$

$$2Al_2OF_4 + 4Na_2CO_3 + \underset{(Anode)}{3C} = \underset{(-)}{4Al} + 8NaF + \underset{(+)}{7CO_2}$$

$$3Al_2OF_4 + 3Na_2CO_3 + \underset{(Anode)}{3C} = \underset{(-)}{4Al} + Al_2F_6.6NaF + \underset{(+)}{6CO_2}$$
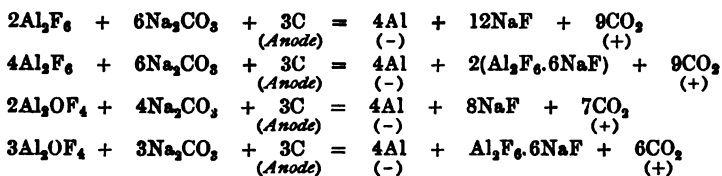
It must be remarked, however, that on merely melting together a mixture of aluminium fluoride and alkaline carbonates, an active disengagement of carbonic acid is observable, probably in accordance with the equation :—

$$Al_2F_6 + 3Na_2CO_3 = Al_2O_3 + 6NaF + 3CO_2$$

So that in this instance it is a solution of alumina in melted alkaline fluoride that is really submitted to electrolysis.

The J. B. Hall Process.—In the year 1893, J. B. Hall (not the C. M. Hall whose patents have been discussed previously) took out a patent * in America for a process in which the old mistake of using a carbon-alumina anode is repeated. The crucible itself is to be used as cathode, and is to be made of the same material, which, on account of its want of durability, must be enclosed within an iron shell. The electrolyte is a fused mixture of aluminium, sodium, and lithium chlorides, in which the bath is replenished at the expense of the alumina contained in the anode. The inventor has also obtained *moderately satisfactory* results (!) by omitting the alumina in the anode composition, and adding it direct to the bath instead. His "new" method of producing alumina is also worthy of note. He treats aluminous material with sulphuric acid, and heats the resulting hydrated aluminium sulphate, thus breaking it up and obtaining the oxide.

Electrolysis of Aluminium Sulphides.—Careful attention should be given to a process, which is protected in Germany by two patents of the same date, and which has for its object the extraction of aluminium from a solution of aluminium sulphide in fused alkaline chlorides. The patent which received the earlier number was granted to Bucherer,† and is concerned mainly with the production of the sulphide, while the other, taken in the name of the *Aluminium-Industrie-Aktien Gesellschaft*,‡ sets forth the advantages accruing from the use of this electrolyte.

Bucherer claims that " by the action of the sulphides or polysulphides of the alkali and alkaline earth metals, with the addition of sulphur and carbon in excess, aluminium oxide or hydroxide, when heated, forms double sulphides of aluminium

* U.S.A. Patent 503,929, Aug. 22, 1893.
† German Patent 63,995, Nov. 13, 1890.
‡ German Patent 68,009, Nov. 18, 1890.

and alkali or alkaline earth metals." The reaction being illustrated by the following equation :—

$$3Na_2S + Al_2O_3 + 3C + 3S = Na_6Al_2S_6 + 3CO$$

In a later account,[*] he describes experiments on the conversion of the aluminium oxide into the sulphide without the agency of other sulphides. A mixture of alumina and carbon was heated to a white heat in clay retorts, and was completely converted into sulphide by means of sulphur vapour, which was allowed to operate for a sufficiently long period, thus :—

$$Al_2O_3 + 3C + 3S = 3CO + Al_2S_3$$
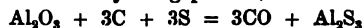
The sulphide so obtained could then be dissolved in a fused alkaline chloride, and could be electrolysed by a current of low electro-motive force.

The *Aluminium-Industrie-Aktien-Gesellschaft* use a similar mixture which is brought to a state of fusion, either by means of the electric current, in which case an E.M.F. of 5 volts is necessary ; or by external heating, when only $2\frac{1}{2}$ to 3 volts will be required for the electrolysing current. Cast or wrought-iron vessels may be used, and they should be lined with carbon. It is claimed as a special advantage of this process that *neither this lining nor the carbon anodes* has any prejudicial effect upon the materials which are here brought into contact with them ; and that on this account, besides effecting a considerable saving of carbon in the various parts of the apparatus, a very pure aluminium is obtained. *The author calls attention to these remarks as confirming his own experience* (see p. 157), *which has tended to show that pure aluminium could not be obtained by using an oxide electrolyte in a crucible made of, or lined with, carbon.*

The behaviour of the sulphide electrolyte is so remarkable, that it is a matter for regret that at present no advantage can be taken of it, because up to the present time no sufficiently cheap method has been invented for the production of aluminium sulphide. It must not be forgotten, on the one hand, that the metal may be obtained directly by electrolysis, and on the other, that the sulphide must first be prepared from the pure oxide, whilst as Bucherer himself points out, there is scarcely a purely chemical reaction known which requires so great an absorption of heat as that above described $(Al_2O_3 + 3C + 3S = Al_2S_3 + 3CO)$. Finally, the author, speaking from the experience of many years in the manufacture of alkali and alkaline earth metal sulphides, points out that the production in gross of pure aluminium sulphide, or of the double sulphides of aluminium and the metals above named, is an exceedingly difficult problem. With the means at present available on a working scale, the possibility of introducing the electrolysis of sulphides for the manufacture of aluminium is bound up with the solution of this problem.

[*] *Zeitschrift für angewandte Chemie*, 1892, p. 483.

Industrial Position of Aluminium Reduction Processes.
—After the foregoing account of the enormous labour bestowed
upon this subject by chemists and technologists in all countries,
it would be only fitting to add a sketch of the present position of
the industry from an economical standpoint; and for this
purpose there is available no lack of published experiences,
but unfortunately they do not originate from the only sources
capable of leading to a true judgment in this matter, namely—
the directors of the larger works. Thus, for example, a few
years since, the actual cost of producing aluminium at the
works, was calculated by an arithmetician at 2s. 9d. per lb.
when the actual market price of the metal was 2s. 3d. The
author's own experiments must, he considers, be deemed of
doubtful utility as affording a basis of calculation, because they
were made with machines of 5 H.P., or under, and could only
be continued at each trial for so long a period as he was able
to superintend them personally without being overcome with
fatigue. None therefore exceeded 36 to 40 hours, even if all
went well from the first. In order, for example, to fix the most
important factor in the calculation, the difference of potential
in the bath, the *most favourable* results would lead to the adop-
tion of 9 to 10 volts as correct; and this with a current density
of about 25,000 amperes per sq. metre of cathode surface [1·61
amperes per sq. in.] would correspond to a yield of at most 1½
lb. of metal per 24 electrical horse-power hours.* It should be
remarked, however, that this calculation is based on the most
favourable results, and not upon an average; but, on the other
hand, it must not be forgotten that in a larger plant there is a
higher thermal efficiency, and that this number is *probably*, after
all, not very different from the average result in large works.

**Summary of Conditions to be Observed in the Extraction
of Aluminium.**—Keeping in mind the deductions drawn from
the experiments of Bunsen and Deville, the foundation of the
modern methods of smelting aluminium may be shortly
summarised as follows:—

1. A solution of alumina in melted haloid salts (chlorides and
fluorides) of the alkali or alkaline earth metals, or of aluminium
itself, is used as electrolyte.

2. The proportion of aluminium in the bath is kept constant
by the addition of alumina during the operation.

* [This is equivalent to 1 oz. per E.H.P. per hour. On the authority of
G. L. Addenbrooke (*Journal of the Society of Arts*, 1892, vol. xl., p. 661),
the yield by the Hall process, as worked in America, at a potential of 8 to
10 volts, is one lb. of aluminium per 22 E.H.P. hours, or about 0·73 oz.
per E.H.P. per hour. Dagger gave the same numbers in 1892 (22 E.H.P.
hours per lb. Al) as "the amount common to the electrical methods now in
operation" (*Journ. Soc. Chem. Ind.*, 1892, vol. xi., p. 128). The Héroult
patent specification, however, quotes 1 oz. per E.H.P. per hour, and this
is in accord with the number given by Richards; but see p. 151 of this
book.—TRANSLATOR.]

3. Carbon blocks, closely united, form the anode, while the cathode consists of a metal tube inserted through the bottom of the melting vessel, and capable of being cooled by water or otherwise.

4. The melting vessel consists of a shallow iron cylinder open above and lined within with pure refractory compounds of aluminium.

5. The heat necessary for fusion is produced by the current that serves for electrolysis, a very high current density being employed, amounting to some 25,000 amperes per sq. metre [1·61 amperes per sq. in.] of cathode area.

6. The walls of the melting vessel must be kept so cool that the lining does not become dissolved in the bath.

7. The temperature of the electrolyte is kept as low as possible, because, apart from the waste of heat energy occasioned by the use of high temperatures, it is probable that the metal may, to some extent, redissolve in the bath in the condition of sub-oxide, this being fully oxidised again at the anode, and so occasioning a waste of metal. The possibility of the separation and volatilisation of alkali metals at high temperatures introduces another source of loss both of current and energy.

Relative Specific Gravities of Metal and Electrolyte.—It may appear astonishing that the aluminium separated by electrolysis from such salts as cryolite, or from solutions of alumina in fused cryolite, should collect on the bottom of the melting vessel, seeing that the usually accepted specific gravities of these substances would lead to the contrary expectation. The specific gravity, for example, of aluminium is taken as 2·7, and that of cryolite as 3. J. W. Richards has, however, experimentally determined the densities of the materials employed both in the molten condition and after cooling. The results, which suffice to explain the apparent anomaly, are given in the following table :—

SPECIFIC GRAVITIES OF ALUMINIUM COMPOUNDS.

	Specific Gravities.	
	Melted.	Solid.
Commercial aluminium, ...	2·54	2·66
Commercial Greenland cryolite, . . .	2·08	2·92
Cryolite saturated with alumina, . . .	2·35	2·90
Cryolite with aluminium fluoride, $Al_2F_6 . 6NaF$ + $2Al_2F_6 = 3(Al_2F_6 . 2NaF)$, ...	1·97	2·96
Same mixture saturated with alumina, . . .	2·14	2·98

Uses of Aluminium.—Although only a few years have elapsed since the price of aluminium has fallen to its present level from one that had always been prohibitive, the metal has already found a wide-spread application for household and kitchen utensils, articles of military equipment, art-work, especially in place of silversmith's work, scientific instruments, and (in the largest proportions of all) for the refining of metals, although the quantity added in each operation is very small. In the iron, steel, and copper foundry, aluminium is used to reduce the oxides present in the melted metals, so that a dense casting free from blow-holes may be obtained, while at the same time the working properties of the purified metal will have become improved. In casting iron it is to be noted that the addition of more aluminium than is necessary to reduce the oxide present in the charge tends to produce a separation of carbon in the form of graphite.

The metal has, however, found but limited application in engineering, on account of its low tenacity, which is not greatly increased by the addition of small quantities of other metals, such as copper. It would otherwise be especially adapted to the requirements of marine and aërial engineering. It is already sometimes used for the construction of the framework, slide-valve, valve and pump chambers of marine engines, and other metallic mountings used on board ship; and recently experiments have been made in the construction of launches and boats from aluminium plate [commonly alloyed with a small percentage of some other metal, such as nickel or copper. —TRANSLATOR].

CHAPTER II.

THE CERITE METALS.

CERIUM, LANTHANUM, DIDYMIUM.

Properties of the Cerite Metals.—The metals of this group have been, up to the present, little used in the arts, at least in the metallic form ; but owing to the wide-spread employment of their oxides for lighting purposes in the incandescent gas-lamp, attention has naturally been drawn to the properties of the metals themselves. The discovery of new cerite deposits, or the publication of the fact that cerite is not so scarce in Sweden as is commonly supposed, might lead to some unexpected application of the metals contained in this mineral.

Cerium (atomic weight = 140; specific gravity = 6·7) is a soft malleable metal, in colour resembling iron, fusing at about 800° C. Most noteworthy is its power of combining with the heavier metals, such as copper or iron, to produce dense alloys. In solid pieces it offers considerable resistance to atmospheric influences; but, on heating the fragments, they exhibit the various temper-colours of polished steel. Finely powdered cerium, on the contrary, oxidises very rapidly in the air, and, on filing the metal or shaving it with a knife, the detached filings or scrapings take fire and burn with a brilliant light. Fine wire made from the metal burns with a brilliancy exceeding even that of magnesium. Cerium in the form of powder causes only a slow decomposition of water when introduced into it, but the presence of salts, dissolved in the liquid, induces a very lively attack. This property should be noted in connection with the production of cerium, and with the possibility, which may easily arise, of obtaining the metal in pulverulent form, owing to the use of an electrolyte at too low a temperature. It dissolves very easily in diluted acids, but only to a slight extent in cold concentrated sulphuric or nitric acids. Cerium reduces the oxides of most metals and metalloids, which is a property worthy of remark in regard to its applications to metal refining and the making of alloys.

Lanthanum (atomic weight = 138·5; specific gravity = 6·1) possesses a colour resembling that of cerium, but it is less soft and malleable than the latter. It shows a tendency during its preparation to separate in the form of thin leaves. Its fusing point is higher than that of cerium. The chemical relations of the two metals are very similar.

Didymium (atomic weight = 142; specific gravity = 6·5) is a clear grey metal, harder, less malleable, and less easily fusible than cerium, but resembling it in its chemical properties.

Preparation of the Cerite Metals.—*The methods of producing these three metals* show but few differences. The statement of the chemical text-books that *the oxides of the cerite metals are not reducible by means of carbon is* incorrect. It has been shown (pp. 88, 111, &c.) that all oxides are capable of being reduced by electrically-heated carbon; but since a large excess of carbon must be employed, combination of the reduced metal with that element is unavoidable. In consequence of this, the production of the cerite metals by such a process does not appear to be promising, for the product is exceedingly brittle, easily crumbled, and porous, and is therefore readily oxidised. The separation of the metal by Wöhler's method (treating the haloid salts with metallic sodium) would probably give better results, especially if a system analogous to that adopted by Grabau for aluminium extraction (p. 103) were employed.

Electrolytic Deposition of the Cerite Metals.—Electro-

lysis, however, seems to offer the best solution of the problem, as in the case of aluminium. The cerite metals appear to form a group intermediate between those of magnesium and aluminium, in regard to the behaviour of those salts which would be likely to come into use for electrolysis. It is well understood that none of the chlorides of these metals can be obtained in the anhydrous condition by evaporating their solutions in water, since decomposition always occurs on drying. But, as in the case of magnesium-chloride, if a chemically equivalent quantity of the chloride of sodium or potassium, together with a little ammonium-chloride, be added, the solution of the cerium, lanthanum, or didymium oxide may be evaporated to dryness, and the dry residue may then be fused without decomposition. The melt then contains comparatively easily fused double chlorides of the cerite and alkali metals, and will be found to conduct the electric current well. But although it may have been easy to obtain the metals of the magnesium group, magnesium and lithium, almost absolutely pure, either by direct electrolysis or by electrolysis followed by fusion, it is not safe, with the methods of production hitherto described, to rely too much on the purity of the separated metal, if its reduction have been effected in quantities somewhat greater than would be possible in the small porcelain crucibles of the laboratory. It is, indeed, very improbable that Bunsen, Hillebrandt, and Norton, who were the first to reduce the cerite metals by electrolysis, obtained a product that was free from iron. They employed the following method, which was devised by Bunsen * :—

The decomposing vessel in which the electrolysis of the molten chloride was to be accomplished, was arranged after the fashion of a Grove's element. The outer cell, which in the Grove's battery contains the zinc plate and sulphuric acid, is here an ordinary Hessian crucible of about 100 c.c. [$3\frac{1}{2}$ fl. oz.] capacity, filled with a fused mixture of equivalent weights of sodium and potassium chlorides, in which a cylinder of thin sheet-iron serves as positive electrode in place of the zinc of Grove's cell. The cylinder is 5 cm. [2 in.] high, and 2·5 cm. [1 in.] across internally, and terminates in a strip which serves as a conductor, and must not be either soldered or riveted in place. Within the cylinder is a clay cell of the best quality, 9 cm. [$3\frac{1}{2}$ in.] high and 2 to 2·6 cm. [$\frac{3}{4}$ to 1 in.] wide, in which is placed the chloride to be decomposed. The negative electrode is immersed in this to about two-thirds of the depth of the cell; the electrode consists of a thick iron wire, the end of which is filed down somewhat thinner, and round its end is twisted a piece of iron wire about as thick as a horse-hair, which projects some 15 mm. [$\frac{9}{16}$ in.] beyond the stouter piece to which it is attached. A piece of a clay pipe-stem is now drawn so far over the thicker

* *Pogg. Ann.*, 1850, vol. clv., p. 633.

wire, that only the fine wire * at the end projects out of the clay and comes in contact with the fused chloride that is to be reduced.

In the reduction of such chlorides as are easily converted into oxides by the action of water vapour, the fusion must never be effected by means of a gas flame. Even in the heating of chlorides that are less readily decomposed, it is better to avoid the use of gas flames, since the water vapour that they evolve is very liable to cause re-oxidation of the already reduced metal. The charcoal that is used to melt the electrolyte in these cells, therefore, must be thoroughly glowing, and should have given off all the hydrogen that it contained before starting the experiment. For the same reason, the chloride that is to form the electrolyte must be very thoroughly dried, and must then be heated in a platinum crucible with sal-ammoniac until the bulk of the latter salt has been expelled. It must be stored in closely stoppered bottles, and be guarded most carefully against the re-absorption of moisture. Finally, when the chloride is melted for the experiment, the contents of the clay cell are covered with a layer of powdered sal-ammoniac, which has previously been heated, and this salt is replaced as fast as it volatilises.

The yield of metal, and the size of the globules obtained, depend upon the temperature at which the fused chlorides are submitted to the action of the currents. If the clay cell be raised to a temperature exceeding the fusing points of the salt under electrolysis and the metal that is to be separated, the drops of metal, which form upon the surface of the negative electrode, fall to the bottom, and are there for the most part re-oxidised at the expense of the silica in the clay walls of the cell. The addition of fuel and the supply of sal-ammoniac are therefore so regulated that the upper part of the salt in the clay cell remains solid, while the lower part around the negative electrode is in a semi-solid or pasty condition. The metallic particles thus increase in size without sinking through the pasty mass, and may even grow into globules the size of a hazel nut if the experiment be carefully tended. The electrolytic decomposition should be started only when the melted salt is in the proper condition, because otherwise the reduced metal is liable to separate in a pulverulent form, and to mingle with the contents of the clay cell, so that the formation of larger metallic globules would be prevented.

The success of the reduction depends not only upon the temperature of the bath, but also upon the absolute intensity of the current employed. Four large carbon-zinc elements suffice for the experiment. The clay cells of such elements should con-

* A piece of this wire, 1 cm. long, weighs about 4 mg. [1 in. weighs about 1½ grain.]

tain 250 c.c. [9 fl. oz.] of nitric acid; the carbon rods should be 21 cm. long by 2·5 cm. wide by 4·5 cm. thick [8¼ in. × 1 in. × 1¾ in.], and the total available area of the zinc surface surrounding the clay cell should be 590 sq. cm. [90 sq. in.].

The author's experiments in the reduction of these metals by electrolysis have only extended to the treatment of a mixture of their chlorides. Hillebrandt and Norton have apparently adhered too carefully to the process devised by Matthiessen for the separation of strontium. It is not necessary in this case to use a current density of the grade that is required for the separation of the alkaline-earth metals. The double chlorides of the cerite and alkali metals above described may quite easily be electrolysed in an iron crucible, which either serves as (or is in direct electrical connection with) the cathode. (See under *Lithium*, p. 34, and *Magnesium*, p. 28). In such an experiment, with a cathode area of 500 sq. cm. [77·5 sq. in.], a current of 50 amperes and 6 to 7 volts should be used. Of the three metals, cerium separates out first in the molten condition; and by stopping the experiment at the right moment, it is possible to obtain this element, almost free from lanthanum and didymium, but containing much iron; it may be separated by pouring off the fluid salts, and then emptying the metal, which remains at the bottom, into a suitable mould. The salt may then be remelted, and on continuing the operation, the didymium is deposited in the form of powder or flakes. The lanthanum precipitates partly with cerium, partly with didymium. This process is, however, as little to be recommended for the practical production of pure metal as that drawn up by Bunsen, even though the chlorides or other haloid salts of the single metals be used in the very purest condition.

The production of a pure metal can only be reckoned upon if an apparatus and a process be used similar to those which are at present employed for the extraction of aluminium; and as the conditions in the two cases are identical, there is no need to repeat what has already been said in treating of aluminium. The circumstance that the salts of the cerite metals may be obtained in the anhydrous state, without the slightest difficulty, greatly facilitates the separation of the metal. The chlorides are obtained, as above described, by evaporating their solutions with alkaline chlorides, and melting the dry residue with an addition of dry ammonium chloride. The fluorides are precipitated in the form of white powder by digesting the aqueous solution of cerite metal salts with fluor spar, or by adding a soluble fluoride to the cerium solution.

Applications of the Cerite Metals.—But little can as yet be written concerning the technical *applications* of the cerite metals. The ease with which cerium alloys with copper and iron, and the great soundness of the alloys produced, and the special reducing

power of the metals (most particularly that of cerium) will become prominent as soon as the supply of cerite is more abundant. If once the metal could be placed upon the market at a cheap rate, there is no doubt that it would at once find a wide field for use in the refining of metals and the making of alloys. A further use in pyrotechny and photography may be predicted for it on account of the extremely brilliant light that it emits during combustion.

PART III.—THE HEAVY METALS.

CHAPTER I.

COPPER.

Properties of Copper.—Copper (Cu; atomic weight = 63·4, specific gravity = 8·94), when pure, exhibits a yellowish-red colour on surfaces recently fractured. The structure of cast copper is granular, but by hammering or rolling it becomes fibrous. It is remarkable for great ductility, united with a moderate degree of hardness and tenacity. Copper which has become hardened by mechanical work may be made malleable again by heating. Its conductivity for heat and electricity is very high, and the latter property has therefore led to its general use for conductors in electro-technical work. Shortly before attaining its melting point (which is about 1050° C.), the metal becomes so brittle that it may be pulverised. In the molten condition the metal has a greenish colour, and it also imparts a green tint to oxidising flames. The boiling point of the metal is not far removed from the temperature of the oxyhydrogen flame, or the electric arc, and may perhaps be taken as approximating 3000° C.

When melted, copper has a great tendency to dissolve certain gases (hydrogen, carbonic oxide, and sulphurous acid), which it evolves again on solidifying. Certain metals (aluminium, nickel, cobalt, zinc, cadmium, tin, lead, bismuth, the noble metals, manganese, chromium, tungsten, molybdenum, and iron) are also readily dissolved by it, as also various metallic compounds (cuprous oxide, sulphide, and phosphide, and the arsenides, arseniates, antimonides and antimoniates of lead, bismuth, &c.). The solubility of the gases and the compounds last named should be remembered in the melting of the copper in the refinery, and in the casting of copper and its alloys generally. The mutual solubility of copper and other metals is utilised in the preparation of alloys.

Of the chemical properties of this metal the following may be specially noted as bearing upon its extraction and useful applications :—The polished surface of rolled or hammered (and

therefore dense) copper may remain unaltered in the air for a long time; but, in contact with acid substances in the presence of air, the metal is very easily oxidised with the formation of basic salts (*e.g., verdigris*). Or, again, at a low red heat, far below its melting point, it becomes covered with a film or "*scale*" which consists of a mixture of the cuprous and cupric oxides.

In combining with sulphur it exhibits a far greater chemical energy than does any of the other heavy metals, and this property has a special interest in connection with the extraction of copper from its ores. Copper also unites directly with the other metalloids, excepting hydrogen, nitrogen, and carbon. A product in which hydrogen is associated with copper is known, but is not commonly regarded as a true chemical compound.

The principal solvents for copper are nitric acid, concentrated sulphuric acid, and *aqua regia.* Hydrochloric acid and dilute sulphuric acid only dissolve the metal when air or some other oxidising substance is present; on account of the low solution pressure of this metal, hydrogen can never be produced by the action of acids upon it, and it is for this reason that the addition of an oxidising agent is required.

Although copper is able to form two compounds with oxygen or with sulphur (cuprous oxide or suboxide, Cu_2O, and sub-sulphide or cuprous sulphide, Cu_2S; and the cupric oxide, CuO, and sulphide, CuS), it produces only one series of salts with oxygen acids,[*] and these are produced from the higher oxide, CuO. Only with the haloid acids can both cuprous and cupric salts be formed. Copper shows a great tendency to form basic salts.

Occurrence of Copper in Nature.—Among the ores of copper, only the following need be mentioned here:—**Native (metallic) copper; red copper ore, Cu_2O; black oxide, CuO; copper pyrites, $Cu_2S . Fe_2S_3$; copper glance, Cu_2S; malachite, $Cu_2(OH)_2CO_3$; and blue carbonate, $Cu_3(OH)_2(CO_3)_2$.** Of these, the sulphides are most used for the extraction of the metal, because they are the most widely distributed; and it is quite exceptional to find native copper, the oxides, and salts smelted alone.

1. **The Roasting Processes.**—The mechanical separation of the cupriferous from the non-cupriferous materials of the ore is limited by the comparatively slight differences between the densities of these constituents, and by their being intimately mixed, alloyed or even chemically combined, so that only a product with but a small proportion of copper may be aimed at. The smelting of such ores, whether raw or dressed, for the direct production of copper, would not only give rise to a great loss of the metal in the numerous bye-products, but would yield a copper that would be worthless for most purposes, unless it were

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[*] [The exceptions to this rule—*e.g.*, cuprous sulphites—are so few in number that they may fairly be disregarded in this book.—TRANSLATOR.]

first submitted to such a process of refining as would involve an expenditure that would be quite prohibitive. Accordingly, the first process in the extraction of copper is always one of chemical preparation or concentration, dependent upon the high chemical stability of copper when it is combined with sulphur in the melted condition. The ore is therefore calcined in order to remove a part of its sulphur by oxidisation, so that, on subsequent fusion, it may yield a matte ($Cu_2S . xFeS$) containing the copper in the form of sulphide. This process is then repeated again and again, if necessary, until the matte contains sufficient copper for use in the smelting furnace. The resultant matte is finally roasted, and is subsequently or simultaneously melted, not only to effect the removal of foreign substances, especially FeO, in the shape of slag, but to enable the oxide of copper that is formed to react with the sulphide already present, and so to yield metallic copper and sulphur dioxide.

In England, such a process was at one time used to the exclusion of all others; and this **Welsh Process**, as it was termed, may be epitomised as follows:—

(i.) *Calcination of the Ore.*—This was originally conducted in simple reverberatory furnaces, and later in mechanically-stirred or revolving furnaces, pyrites-burners,* or the like, the object being to recover the sulphur from the gases by converting it into sulphuric acid, whilst at the same time so reducing the proportion of sulphur in the ore that the latter might, on melting, yield an easily fusible matte consisting of complex sulphides containing a proportion of copper much larger than the initial average of the charge. So far as the substances taking part in the principal reactions of the smelting process are concerned, the calcined ore may be said to consist of a mixture of the oxides and sulphides of iron and copper.

(ii.) *Melting for Coarse-Metal.*—The calcined ore is melted in a reverberatory furnace, so that a matte (coarse-metal) may be obtained, which contains practically the whole of the copper combined with a portion of the sulphur as sulphide, together with as much sulphide of iron as may be formed by the remaining sulphur in the charge. The excess of iron is in the form of oxide, and as it is fluxed by a suitable (acid) addition of silica to the charge, it is carried away in the resulting slag.

(iii.) *Calcination of the Coarse-Metal.*—As in the first calcination process, a part of the residual sulphur is removed, but there must still be left in the calcined charge enough (or slightly more than enough) sulphur to combine with the whole of the copper present.

* For descriptions of other forms of plant which are not employed in electro-metallurgical work, the reader is referred to the text-books on metallurgy; or for those of calciners used in connection with vitriol chambers to the hand-books of the alkali trade.

(iv.) *Melting for Fine-Metal.*—The calcined charge from the previous operation is melted in a reverberatory furnace with an acid bottom, and thus, by reactions resembling those of stage (ii.), affords a concentrated matte (fine-metal), which should be nearly pure sulphide of copper. If the matte should be too impure it must be remelted; but this is rarely necessary if the Welsh process have been properly conducted; and it is generally passed on to the roasting process.

(v.) *Roasting for Blister-Copper.*—This operation* is now performed either in two separate stages—roasting and reaction—or in one operation. In the former case the fine metal is roasted in a reverberatory furnace, and then melted, so that the reaction of copper oxide and sulphide above-described might lead to the production of crude metallic copper (blister-copper). Foreign oxides were as far as possible removed by the addition of acid fluxes, reacting upon an acid hearth.

The older process of roasting in a reverberatory furnace is now replaced at many works by that of Bessemerising. As the name suggests to any who are acquainted with the original Bessemer process, this operation consists in forcing a powerful blast of air through the melted matte, when the same chemical reactions will take place as occur in the roasting process. Owing to the low specific heat, and the good thermal-conductivity of copper, there would be great risk [amounting to a certainty] of the separated copper solidifying at the bottom of the converter, if this vessel were made on the precise pattern of those used in steel making. The twyers for the admission of the air-blast must therefore be placed above the level of the melted copper, instead of at the bottom of the converter. In some instances these converters are made in the form of horizontal cylinders, resembling revolving calciners, with the twyers placed in a horizontal line, so that their level may be altered to correspond with the progress of the reaction, whilst in other cases the shape of the original (steel) converter is retained, but the twyers are placed around the sides instead of at the bottom. The lining is of an acid character.

In the Welsh process only sulphide ores can be used, but oxides or oxidised ores or products may be introduced in some of the operations in place of calcined ore.

2. **The Reduction Process.**—This process is usually applied to the smelting of sulphide ores, and, therefore, necessitates a preliminary concentration for the reasons already adduced. The processes formerly used in Germany and Sweden (and sometimes

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* [In the latest modification of the Welsh process (by Nicholls and James), a portion of the fine metal is roasted, and is then melted with so much of the unroasted fine metal that the above reaction takes place quantitatively, and practically no slag is produced. The refining process is then at once effected in the same hearth.—TRANSLATOR.]

known as the German or Swedish processes) differ from those employed to-day only in the character of plant, and in the working details connected with the use of the latter. The chemistry of the newer system of work remains unchanged, and it will, therefore, suffice to give an outline of the modern process as follows :—

(i.) *Roasting of the Ore.*—This is usually effected in pyrites-burners, or similar apparatus, if sulphuric acid is to be obtained as a bye-product; but otherwise in reverberatory furnaces, with mechanical stirrers or in revolvers. The chemical changes involved have already been explained.

(ii.) *Melting for Coarse-Metal (Rohstein).*—This is conducted almost exclusively in low blast-furnaces 20 to 30 ft. high, and affords a matte containing 35 to 40 per cent. of copper.

(iii.) *Roasting the Coarse-Metal,* for the most part in kilns.

(iv.) *Melting for Fine-Metal (Spurstein).*—The operation was formerly performed in blast furnaces; but reverberatories are generally employed at present, giving a matte which should contain about 60 to 70 per cent. of copper.

(v.) *Dead-roasting of the Fine-Metal,* first in kilns, and subsequently in heaps.

(vi.) *Reduction of the Roasted Fine-Metal.*—In the old German process this part of the work was done in low blast furnaces, but these have been replaced by reverberatory furnaces. The product of this operation is known as black copper (*Schwarz-Kupfer*).

The presence of certain other metals in the ores will obviously necessitate alterations in the above practice, or the introduction of intermediate processes to which allusion will shortly be made. This method is principally adapted to the smelting of sulphide ores; and it is unnecessary to point out that roasting processes need not, as a rule, be applied to oxidised ores and metallurgical products, such as red copper ore, carbonates, or silicates, which may be *smelted for pure metal immediately,* and usually in the blast furnace. The fluxes added to the charge in this case must of course be suited to the nature of the gangue stuff and the copper minerals operated upon; they must usually have a basic character, however, for example: dolomite, basic slag, and the like. Only exceptionally can substances to be smelted be so selected that the impurities in the one may exactly flux those in the other.

3. **Leaching of Copper from Ores and Furnace Products.** —In the few instances in which the copper is present in an ore in a soluble form (*e.g.,* copper sulphate), the application of this process is, of course, very simple. Oxides and carbonates are also very well adapted to this process, suitable solvents being hydrochloric acid, chloride solutions, and sulphuric acid. But even ores which contain less easily soluble compounds of copper are

often treated by the so-called wet methods, if the ordinary smelting processes are not available owing to the small proportion of copper present. The sulphate or chloride of copper is produced by weathering, by an oxidising or chloridising roast, or by treatment with recognised oxidising or chloridising agents, such as ferric salts, cupric chloride, and the like. This substance can then be easily extracted by means of water or dilute acids. From such solutions the copper is separated as cement copper, whenever possible, by treatment with scrap-iron; or, exceptionally, it may be obtained as sulphate or hydroxide.

So also black or finished copper containing the precious metals was at one time ordinarily treated by a process of solution; but this is now done only in the few instances in which the demand for copper sulphate makes the operation remunerative. For this purpose the copper is granulated and placed in a lead-lined wooden vat, where it is subjected to the joint action of air admitted constantly from below, and moderately dilute sulphuric acid poured over it intermittently from above. The effect of the latter is to dissolve the oxide formed superficially by the action of the air, and to rinse off the slime consisting of the precious metals, lead oxide, and other insoluble substances. The latter substances collect at the bottom of the channel through which the copper sulphate solution is run off, and are removed, washed, dried, and submitted to a process of separation, as described in the chapters on silver, gold, and lead. The copper sulphate solution is then crystallised. Formerly the copper liquors were treated with iron, but now, in the absence of any demand for copper sulphate, they are decomposed electrolytically.

4. Refining Processes for Native and Crude Copper.— Occasionally, but very rarely, native copper is found in such quantity and so pure that it may be simply melted, with suitable fluxes to effect the removal of the gangue stuff, and then refined. The smelting processes above described afford only an impure metallic copper (blister, black, or cement copper), which can very rarely be used without further treatment. The impurities contained in these varieties of copper may comprise—silver, gold, zinc, lead, bismuth, cobalt, nickel, iron, sulphides, arsenides, antimonides, &c.

In the first place, the presence or absence of the precious metals influences the choice of a refining process. In their absence the metal is always first submitted to an oxidising roast on the hearth of a reverberatory furnace with an acid bottom. In this way the impurities are removed, either in the slag or by volatilisation; but at the same time it is impossible to prevent some oxidation of copper, a part of the oxide formed remaining dissolved in the otherwise pure metal. The metal at this stage is known as *dry copper*, and is quite useless for rolling or other

mechanical treatment, by reason of the cuprous oxide that it contains, although it might be occasionally used in the manufacture of a few alloys, such as brass. To render it malleable, the cuprous oxide must be removed; and this is most conveniently done by the application of reducing agents after the roasting is complete and the oxide slag has been withdrawn. Accordingly, the melted metal is covered with a layer of anthracite, and is then poled by the introduction of a wooden stake plunged beneath its surface. The gases evolved by the distillation of the wood are themselves reducing, and by stirring the copper into intimate mixture with the anthracite, they cause the reduction of the oxide. When this action has proceeded sufficiently far, the metal is ladled into ingot moulds, and is known as tough-cake copper.

ELECTROLYTIC METHODS OF TREATING COPPER.

On account of the greater simplicity of the electrolytic refining processes, these will be considered before referring to the electrolytic treatment of ores and metallurgical products.

ELECTROLYTIC REFINING OF COPPER.

Early attempts in the Electro-Deposition of Copper.— Although the fact that copper could be separated from its solutions by means of the electric current, was known through Cruickshank's[*] researches in 1800, no successful application of this observation could be made in the field of metallurgy until after the invention of the dynamo. Following upon this, however, no time was lost in utilising the current for the purpose in question.

Attempts, however, were constantly made to apply the current to metallurgical purposes, and especially to the treatment of copper ores, even at a time when there was no economical generator of electricity available. Becquerel's work in the years 1835 to 1840, on the electro-chemical treatment of ores containing silver, copper, and lead, will be referred to briefly under *Lead.* As soon as Jacobi's discovery of electrotyping became known in the year 1838, Smee recognised how important a part electrolysis was destined to play in metallurgy, as may be gathered from his work on electro-metallurgy.[†] Even in 1867, the year in which Siemens first described his dynamo-electric machine, Patera[‡] published an account of a method for the precipitation of copper from cement waters, in which he wrote:—

[*] Nicholson's *Journal of Natural Philosophy*, 1800.
[†] Smee's *Electro-metallurgy*, 1841.
[‡] *Verhandlungen der k. k. geologischen Reichsanstalt*, 1867, No. 5; and *Dingler's Polytechnisches Journal*, 1867, vol. clxxxiv., p. 134.

Patera's Process.—"In a trough lined with guttapercha plates, a rectangular clay cell was so cemented, that the two walls that were in contact with the longer sides of the trough, made a water-tight joint with them; an empty space was thus formed, bounded by the shorter sides of the trough, the free walls of the clay cell, the bottom of the trough and that of the cell. This space was filled with granulated copper, and through it was passed the solution from which copper was to be recovered. Within the clay cell were parallel iron plates, so soldered on to a stout copper wire that there was a space of about four lines between each pair of plates. This system of iron plates was brought into electrical connection with the granulated copper by means of a copper wire. The copper sulphate liquor was continually introduced on one side of the cell, and was run off from the other through a glass tube. A solution of blue vitriol, with a proportion of copper equal to that of the Schmöllnitz mine waters—viz., $\frac{4}{10}$ oz. per cb. ft.—loses more than half its copper in traversing even the $1\frac{1}{2}$ ft. of space through which it has to pass in this small apparatus. By passing the liquid through two such cells in succession, or by leaving the solution in one cell for only a short time, the extraction of copper will be complete.

"It appears, therefore, that this apparatus will answer all requirements. The copper obtained in this way will be very pure, the consumption of iron will correspond very nearly to the equivalent of the copper separated, and the apparatus will be very compact, and therefore easy to supervise. The only difficulty that I [i.e., Patera] observe is that a large quantity of granulated copper must be employed, which, although it is not permanently lost, is locked up in the apparatus, and, therefore, adds considerably to the capital outlay in making the installation. *I afterwards attempted to replace the copper by fragments of coke, and apparently with complete success, for the copper coats the fragments so thoroughly and so easily that they are able at once to form a perfect substitute for the granulated copper.*"

The Elkington Patents.—Elkington's process possesses great interest in connection with copper refining, as it was the first to utilise the current from the dynamo. The English patent* dates from the year 1865, the American† bears a considerably later date. The following is a transcript of the later British specification, omitting preliminary matter:—

"This invention has for its object improvements in the manufacture of copper and in separating other metals therefrom.

"For this purpose I smelt the copper ore so far as to obtain an impure metal therefrom, which I then cast into plates, and by means of electricity I dissolve these plates and deposit the pure copper on to other plates. The other metals with which the

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* English Patent 2838, Nov. 3, 1865; and 3120, Oct. 27, 1869.

† U.S.A. Patent 100,131, of Feb. 22, 1870.

copper was combined fall for the most part to the bottom of the vessel in which I operate. This process in its general outline as above stated is not new, for it has before been patented and used by me, see patent dated November 3rd, 1865, No. 2838.

"My present invention consists in improvements in the method of conducting this process. I prefer to employ copper ores which contain sufficient silver materially to injure the copper if smelted in the ordinary way, and which, consequently, would usually be submitted to a process for extracting the silver before they are smelted. In such ores, frequently, the quantity of silver is not such as to pay for the cost of extraction, but the process has, nevertheless, been necessary when copper of high quality is required to prevent injury to the copper. These ores are particularly suitable for my use as the silver they contain, which does not raise their price in the market, is recovered by me without any additional cost. Ores containing a larger quantity of silver, say from 8 ounces to the ton and upwards, and which are now always submitted to a process for extracting the silver before they are smelted, can also be advantageously worked by my process, as can also ores containing little or no silver, but in this latter case the advantage of my process over the ordinary process is mainly in the better quality of copper which I obtain. I smelt the ore in the usual way so as to obtain all its metallic contents (except such as may be volatile) in the form of a regulus, from which stage, by preference, but it is not essential, I carry the metal on to the state of pimple or blister copper; this impure metal I cast into plates, say 2¼ in. long, 8 in. wide, and 1 in. thick. One end of the plate is provided at the centre with a stout T-shaped head of wrought copper; it is placed in the mould in which the plate is cast. Cast-iron moulds are used. The metal is tapped out of the furnace on to a sand floor, and is led by channels into the moulds. The plates thus cast are ready to go to the dissolving house, which is laid with a wooden floor, inclined from end to end ½ an inch to the foot. The boards are grooved on their edges, and small strips or tongues of wood are inserted into the grooves so that there may be no open joints, and the surface is thoroughly saturated and coated with pitch to make it watertight. The surface of the floor is divided into a number of troughs running from end to end of the building by ledges of wood fixed down upon it ; these are also saturated with pitch. Each trough is of a width to receive three stoneware jars side by side. The jars are cylindrical, 34 in. high and 18 in. wide. There are pathways between the troughs for the workmen who attend to the process. Each trough is filled from end to end with jars. There may be, say, about 100 jars in each trough, and 12 troughs in the width of the building. The jars should be of fire-clay ware so that they may not be injured by the solution which they receive. Each

has a hole in the bottom, closed by a wooden plug, also a hole in the side 4 in. from the bottom, and another hole diametrically opposite to the first and 4 in. from the top. The jars are set up level on the inclined floor with wooden wedges saturated with pitch. The jars are connected together from the upper to the lower end of the room, each jar having a pipe passing out from it at the hole near the top and entering the next jar below at the hole near the bottom. The connection with the jars are made with vulcanised india-rubber, and intermediate of the connections the pipes may be of lead, and about $\frac{1}{2}$ in. internal diameter.

"The solution which I employ is water charged with as much sulphate of copper as it will dissolve. The sulphate of copper of commerce may be used, or for economy I sometimes use a solution obtained by boiling the deposit found in the culvert or long flue by which the smoke from the copper furnace is led to the high chimney; this will furnish a solution of sulphate of copper sufficiently pure for the purpose.

"The solution is stored in a tank at the upper end of the dissolving-room; it is admitted into the uppermost jars, and runs from jar to jar until those at the lower end of the building are filled. Clips are put upon the india-rubber connections to stop the flow through the tubes when the jars are full, and so to maintain the solution at the proper level in the upper jars.

"When the process is in operation two (sic) clips are taken off, say, once in 24 hours, so as to cause the solution to flow through all the jars and transfer the solution from the bottom of one jar to the top of the next, so as thoroughly to mix it, as in working it tends to become weak at the top of the jar. This means of readily equalising the density of the solution is of great practical importance. At the lower end of the room is a tank to receive the solution. When it is thus allowed to run through it is pumped back into the upper reservoir. The same tank receives the contents of the jars when they are emptied on to the floor beneath by the removal of the bottom plug, as hereinafter described. In the gangways between the floor-troughs a truck runs to carry the cast copper plates to the jars in which they are to be dissolved. Six metal plates are suspended in each jar; they are hung in couples from the horizontal copper bars, having forks upon them to receive the T-form heads of the plates. These bars rest at their ends on other bars of wood laid on the jars so as each to extend across a row of three jars, and the same bars also support over each jar two other metal cross-bars to support plates to receive the deposit of copper from the solution. There are four receiving plates in a jar, two suspended from each bar; they are interposed between the cast plates. Conducting strips of sheet copper are laid upon the wooden bars so as to couple the cast plates of one jar to the receiving

plates of the next jar, and so throughout the series of, say, 100
jars. Each metal cross-bar is made to bear on a connecting
strip at one end, and at the other on a wooden block saturated
with pitch. The jars are each provided with a false bottom of
wood to prevent breakage of the jar in case a plate should fall.
The receiving plates may be of wrought copper, but I prefer to
employ in the first instance guttapercha coated with bronze
powder. As soon as a deposition of copper is obtained the
guttapercha is stripped off and the copper left to receive a
further deposit. A series of, say, 100 jars being thus coupled
up into a circuit I connect to the terminals of the series one
or more electro-magnetic machines. I prefer to employ the
machines manufactured by Messrs. H. Wilde & Co., of
Manchester. The machines called by the makers 3½-in.
machines are those which I use, and I drive them at 2500
revolutions per minute. With three such machines working
into a series of 100 jars a deposition of 4 or 5 lbs. of copper in
each jar may be obtained in 24 hours without injury to the
solution. When the cast plates become so far dissolved as to
be unfit for further use they are removed; their remains are
washed in the lower solution tank to remove the deposit from
their surfaces, and they are melted and recast. The wrought
T-heads may be used an indefinite number of times, as I protect
them from solution by coating their stems with wax. The
receiving plates are allowed to grow until they attain a con-
venient weight; they may either be melted and cast into cakes,
and afterwards rolled in the usual way of working copper, or the
plates, as they come from the vats, may be sent into the market.
The solution may be worked for a very long time, evaporation
being supplied by the addition of water acidulated slightly with
sulphuric acid, and ultimately will become so charged with
sulphate of iron as to make it inconvenient to work it further.
If, however, the metal be advanced to the pimple or blister stage
before casting the plates it will take but little iron into the
solution. The silver or other metals (excepting the iron) with
which the copper of the cast plates was contaminated, sinks to
the bottom of the jars and is there allowed to accumulate until
it reaches the lower side hole; when this happens the bottom
plugs are taken out of all the jars of the series, and the contents
washed out into the floor trough, which discharges them into
the tank at the end of the building; here they settle, from time
to time the tank is pumped dry, and the sediment is taken out.
There are two such tanks at the lower end of the room to allow
of one being put out of use before emptying.

"The sediment may be treated in any ordinary and well-
known manner for the recovery of the silver it contains, and
other metals may be separated from it should it be considered
desirable to do so."

Excepting the form of the decomposing vessels, which is a little unpractical, and the method of arranging the electrodes, which is lacking in simplicity, this process is one which exhibits all the essential features of the modern methods of copper refining; and it must be admitted that Elkington well understood how at once to turn to his advantage the discoveries in electro-technology.

Theory of Electrolytic Copper Refining.—The process as it is practically applied consists, then, in the electrolysis of a copper sulphate solution with anodes of crude copper and pure copper cathodes. And whether the phenomena observable in carrying out the process be interpreted by the old explanation, or by the new, it will be found that no great expenditure of power can theoretically be necessary to carry over the copper from the positive to the negative electrode. According to the older view the electric current serves to decompose the electrolyte ; and it would therefore first cause the transposition shown in equation (i.) :—

$$\text{(i.)}\quad CuSO_4 + H_2O = \underset{(-)}{Cu} + H_2SO_4 + \underset{(+)}{O}$$

But then at the same time there would be occurring an oxidation and solution of copper at the anode, with a reproduction of the original electrolyte, and therefore a reversal of the former equation, thus :—

$$\text{(ii.)}\quad Cu + H_2SO_4 + O = CuSO_4 + H_2O.$$

On calculating the E.M.F. necessary to these reactions from the thermo-chemical data indicated by the two equations, it will be seen that the one balances the other, and the resultant is *nil*.

According to the modern explanation the electrolytes are entirely or in part dissociated. In such a case the solution must contain equivalent Cu'' ions and SO_4'' ions. The solution is nearly saturated, and the osmotic pressure is therefore more favourable to the separating out of dissolved substances. But another characteristic of copper refining is that large quantities of copper are transported from the anode to the cathode. It is true that the copper of the anode possesses a solution pressure, even if it be but small ; but equilibrium is maintained without any further expenditure of energy by the back osmotic pressure of the cations already existing in the solution. But even a slight excess pressure, produced outside the bath by the dynamo, which is in direct metallic connection with the electrodes, serves at once to set in motion large quantities of copper on their path from the anode to the cathode, where an escape is of course provided for the electrical charges given up by the copper ions as they deposit.

Theory and practice alike teach that only a very small electromotive force is required to drive copper over from the anode to

the cathode, leaving its impurities behind at the anode, and that, therefore, the quantity of electricity that it is arranged shall be carried by the copper ions must be very large in proportion to the E.M.F.

But in calculating the potential required, it must be remembered that the copper anodes are not composed of pure copper; they contain a considerable proportion of foreign matter which, if left insoluble, is capable of producing polarisation. For this reason the anodes and the electrolyte, and therefore the necessary E.M.F. also, will alter from the very beginning of the operation. Kiliani, in the year 1885,* undertook the task of accurately examining and recording the behaviour of the impurities present in copper under electrolysis. With reference to the conditions of work in this method of refining, he writes :—

Kiliani's Experiments in the Behaviour of Impurities during the Electrolytic Refining of Copper.—"With a normal current density of 20 amperes per sq. metre [1·8 amperes per sq. ft.], and a solution containing 150 grms. copper sulphate and 50 grms. of sulphuric acid per litre [1·56 lb. copper salt, and 0·52 lb. acid per gallon], *cuprous oxide* in the anode remains unaltered, because it is a very bad conductor, and passes at first into the slime or mud left at the electrode; secondarily, however, it gradually dissolves in the acid of the bath, and thus passes into solution at a rate proportional to the time that it is left in the liquid. The presence of cuprous oxide in the anode, therefore, causes the bath to become less acid but richer in copper.

"*Sulphide (or selenide) of Copper* passes as such into the slime, so long as it is not present in quantities which would be considered abnormal in black copper, and especially if it exist in the form of sub-sulphide (Cu_2S). Sulphur cannot then be extracted from the slime by means of carbon bisulphide. It is only when the anode contains a considerable proportion of sulphide, as in the case of matte, that this compound is decomposed with separation of sulphur.

"*Silver, Platinum, and Gold* remain completely in the form of powder in the slime, provided that they be not present in very considerable proportion, and that the solution contain the normal charge of copper and acid. If, however, the solution should become neutral, the silver will rapidly pass into solution, and will then, of course, be deposited at the cathode.

"*Bismuth and Bismuth Oxide* in part pass directly into the slime and in part dissolve into the solution, from which they separate almost completely, in course of time, in the form of a basic salt.

"*Tin* at first dissolves in the bath, but partly deposits again on

* *Berg- und Hüttenmännisches Zeitung,* 1885, p. 249.

standing, as a basic salt; but if much of this metal be present in the anodes, the greater part will be left as basic sulphate on the anode itself.   In the moist condition, this anode slime has a dirty pale-grey colour, but on drying in the air it becomes white, and increases rapidly in weight, even after long drying at 100° C., so that it is almost impossible to weigh it correctly. Finally, the slime contains, besides sulphuric acid, tin oxide, which is present almost entirely in the form of the α-stannic acid, soluble in hydrochloric acid, and only in very small proportion as the β- (meta) stannic acid, which is insoluble in that liquid.   The presence of tin, therefore, causes the bath to become weaker in respect of copper, without gaining any considerable proportion of tin in exchange; and in consequence of the separation of the basic salt, the liquid becomes slightly, but quite appreciably, more acid.

" But the presence of the tin in the solution appears to exert a remarkably favourable influence upon the deposit of copper; for, whilst a bath consisting of a chemically pure neutral solution of copper sulphate gave with the above-named current density a deposit that was exceedingly bad, warty, and brittle, the same current produced an exceptionally good copper, free from wart-like protuberances, and very malleable, when the anode contained a notable proportion of tin.   This favourable result was obtained even when no trace of tin was to be found in the electro-deposited copper; it was tested for by dissolving the deposit in nitric acid, evaporating, and re-dissolving the residue in acidulated water, and not the slightest precipitate, or even turbidity, indicative of the presence of tin, could be observed in the resulting solution.   From the observation of this phenomenon, no doubt, arose the custom, practised by a few electrotypers, of adding tin salts to their baths.   The E.M.F. required for the electrolysis is also markedly reduced when fairly large proportions of tin are present in the anodes.

"*Arsenic* dissolves in either acid or neutral solutions as arsenic acid, until the solution is saturated with the latter, and then it remains undissolved in the slime.   The arsenious acid, combined with cuprous oxide or other metallic oxides, passes entirely into the slime if the solution be neutral, because these compounds are not conductors of electricity.   If, however, the electrolyte be acid, a secondary (purely solvent) action takes place, and the arsenic slowly dissolves into the bath in the form of arsenious acid; but this solution, of course, takes place in a less degree the more often the action of the acid is stopped by lifting the anodes from the vat and removing the slime from their surfaces.   The influence of the arsenic in the anode copper is, therefore, to make the bath poorer in respect of copper, but richer in acid.   The copper deposited from neutral arsenical solutions will contain arsenic, but that from acid solutions will

be free from this impurity unless the bath contain proportionately very little copper.

"*Antimony* goes partly into solution whether the bath be acid or neutral, and in part remains as basic sulphate at the anode, whilst a portion of that which dissolves separates out again on long standing. The antimonial anode-slime behaves like that containing tin, in that it gains in weight on exposure to the air. Antimony, therefore, makes the electrolyte poorer in copper. The antimoniates are not decomposed by the current, and therefore remain at first in the slime; they are, however, gradually attacked by the acid of the bath with separation of antimonic acid, and so tend towards the neutralisation of the electrolyte; but, of course, this effect is the least marked when the slime is the most often removed from the bath. Even when the solution is saturated with antimony, and basic salt is becoming precipitated in the vats, the antimony is not deposited at the cathode so long as the electrolyte contains approximately the normal proportions of acid and copper; at the worst, some basic salt may in such a case mechanically adhere to the cathode in the shape of a black muddy deposit containing copper and antimony. But if the solution should be nearly or quite neutral, antimony will come down with the copper, and the deposit will be dun-coloured and brittle, and will often be characterised by long needle-like excrescences, bounded by rectilineal planes. So too, if the electrolyte contain too little copper salt, even the usual proportion of acid will not prevent the antimony being precipitated with the copper

"*Lead,* under the action of the current, is attacked even before the copper, and passes into the slime as insoluble sulphate, only traces going into solution, without any tendency to deposit at the cathode. The presence of lead in the anode, therefore, makes the bath proportionately poorer in copper.

"*Iron, Zinc, Nickel,* and *Cobalt* dissolve under the action of the current more readily than copper, and, therefore, weaken the solution in respect of the latter metal. But besides this, when small current densities are employed (as they are in copper refining) a simple chemical action takes place between these metals and the free acids present, which results in a greater solution of such metals at the anode than is equivalent to the copper deposited at the cathode; the bath, therefore, loses in free acid, but contains in exchange a greater proportion of metallic salts.

"*Iron* always forms a ferrous compound on dissolving when the current density is small, but this is gradually peroxidised to the ferric state under the influence of the air during the circulation in the vats; and this reaction also tends to a neutralisation of acid. Ferric salts are formed at the anode itself only when a high current density of about 1300 amperes per sq. metre

[120 amperes per sq. ft.] leads to a separation of oxygen and free acid at that electrode. Sulphide of iron at the anode forms only ferric salts. Even if all the copper in the solution be replaced by iron, excepting about 2 grms. per litre [⅓ oz. per gall.], warty excrescences will still be formed.

"The mud or slime deposited at the anode may contain, after drying, gold, platinum, silver, silver sulphide, cuprous oxide and sulphide, basic sulphates of bismuth, tin and antimony, antimonic acid, arseniate of copper, metallic arseniates and antimoniates, lead sulphate, and slag constituents, in which may be iron, lime, magnesia, and silica; and with these there will also be a certain amount of metallic copper in pulverulent form. The gradual solution of the anodes does not always so take place that the innermost portions are only attacked when the outer surfaces have been completely dissolved; on the contrary, it happens much more frequently that the solvent action penetrates far into the interior of the anode while there is yet much copper at the surface. Brittle black copper plates, for example, containing 96 per cent. of copper, 2·5 mm. [$\frac{1}{10}$ in.] thick, were submitted to electrolytic solution, and even after ten days in the bath they had become so soft throughout that they could be rolled together like cardboard without breaking. Anode plates cast direct from copper pyrites always exhibited a marked bulging towards the cathode after a few days in the electrolytic tanks. The electrolyte itself usually becomes weaker in respect of acid and copper, whilst taking up iron, zinc, nickel, cobalt, manganese, tin, arsenic, antimony, and bismuth, and it then shows a higher total proportion of metallic salts.

"The last-named disadvantage is, however, to some extent, compensated by a bye-reaction; for it always happens, in the treatment of comparatively pure samples of crude copper, that the solution becomes gradually richer in copper, without sufficient evaporation taking place to account for the phenomenon. It is a well-known fact that copper is able to exert a slight reducing influence on acid solutions of copper sulphate with the formation of a little cuprous salt, which then, under the action of the air, becomes reconverted into cupric sulphate. This peculiarity was studied by H. Roessler,* and formed the ground work of the older sulphuric acid process of treating copper. This bye-reaction leads to a slight but continuous solution of copper, which is always the more marked as the current density is reduced, and the circulation of liquid is made so much more rapid, that the solution is brought into better contact with the air. The solvent action thus caused is most marked in the neighbourhood of the upper surface of the bath, and may be so great that a thin cathode plate projecting above the electrolyte will be completely cut through at this level in the course of

* *Dingler's Polytech. Journal,* ccxlii., 1881, p. 286.

eight days. This bye-reaction explains the fact that the loss of weight at the anode is greater, and the gain at the cathode is somewhat less, than they should be respectively if they corresponded to the current strength employed.

"*It is therefore very important that the percentage of acid in the bath should be determined from time to time, and that any deficiency should be made good.* And it is equally necessary that the proportion of copper shall not be allowed to fall too low. The most favourable current-density is 20 to 30 amperes per sq. metre [1·8 to 2·8 per sq. ft., or 0·013 to 0·019 amp. per sq. in.].

"The gradual neutralisation of the solution produced by the operation of the various reactions above alluded to, has the most detrimental influence on the whole course of the electrolysis. In the first place, the conductivity of the electrolyte is greatly diminished, and the difference of potential required between the electrodes, under otherwise normal conditions (with the electrodes 5 cm. [2 in.] apart), may have to be raised from 0·1 to 0·25 volt, solely on account of this neutralisation. Then the impurities present in the bath are liable to pass into the cathode deposit as already explained, and to make it brittle and useless. But apart from the introduction of impurities, the deposit obtained, even from a chemically pure solution, is exceedingly unsatisfactory if the liquid be neutral; and it may in fact be so brittle that it can be crushed to powder in a mortar. The cause of this trouble is the formation of cuprous oxide. When the current density is small, the current does not decompose the copper sulphate completely into metallic copper and SO_4, but it deposits a certain proportion of cuprous oxide as well, and the amount of the oxide diminishes as the current density is increased, until at a certain limiting point pure copper is deposited alone. In acid solutions this cuprous oxide becomes decomposed by a secondary, or chemical, action, whereas in neutral liquids it remains attached to the cathode.

"A good circulation of the electrolyte is also an essential since, otherwise, the upper portions of the bath will be more or less denuded of copper, and impurities will in consequence be deposited on the corresponding portions of the cathode. The influence of the circulation on the potential in normal solutions cannot well be measured; but the E.M.F. required increases markedly with any addition of impurities. This is shown by experiments, the results of which are quoted in the following table. In these, cathodes of pure copper were used, with a distance of 5 cm. [2 in.] between the electrodes, and a current of 20 amperes per sq. metre [1·86 amperes per sq. ft.]. The black copper anode used contained per cent.—96·6 of copper, 0·403 of silver, 0·011 of gold, 1·23 of arsenic, 1 of iron, and 0·54 of sulphur.

TABLE SHOWING EFFECT OF IMPURITIES ON THE E.M.F. REQUIRED
FOR THE ELECTRO-DEPOSITION OF COPPER.

| 1000 parts of solution (by measure), contained. | Anode. | E.M.F. in volts. | |
		With circulation of solution.	Without circulation of solution.
Weight. 150 parts copper sulphate, 50 ,, sulphuric acid,	Pure copper, . .	0·095	0·095
	Black copper, .	0·120	0·120
	Copper matte, .	0·400	0·400
150 parts copper sulphate,	Pure copper, . .	0·240	0·243
	Black copper, .	0·275	0·278
	Copper matte, .	0·532	0·535
7·96 parts copper sulphate, 158·2 ,, ferrous sulphate, 50·0 ,, sulphuric acid,	Pure copper, . .	0·22	0·75
	Black copper, .	0·25	0·75
	Copper matte, .	0·50	1·00
7·96 parts copper sulphate, 158·2 ,, ferrous sulphate,	Pure copper, . .	0·30	1·10
	Black copper, .	0·35	1·15
	Copper matte, .	0·75	1·30

" The absence of circulation in the solution, however, not only necessitates an increase in E.M.F., but it exerts a most serious influence upon the physical and chemical properties of the copper deposit; for this is always purer, more finely crystalline, and more malleable in proportion as the liquid is well stirred, even when perfectly pure solutions are used, and otherwise normal conditions observed.

" In order to calculate the expenditure of energy necessary for the treatment of a given raw material, a laboratory experiment must be made in which the difference of potential between the two electrodes is measured, when they are separated by a space equal to that which will divide them in practice, and when they are subjected to the same current density that has been proved the most favourable on the large scale. If, then, for example, the interpolar E.M.F. of the dynamo be 15 volts, and that required for each pair of electrodes be 0·25 volt (neglecting for the moment the external resistance of the vat connections), it should be possible to couple at most (15 ÷ 0·25 =) 60 pairs in series; but this number is never attainable in practice, and on an average 40 baths so arranged would be the more probable practice. If now the dynamo afforded a current of

240 amperes at the above voltage, corresponding to a deposit of 283·61 grms. [0·625 lb.] of copper per hour, there would then be obtained in all the 40 baths arranged in series a total of 11,344 grms. [25 lbs.] of copper in one hour, or 272·26 kgs. [600 lbs.] in 24 hours. The power required to accomplish this is $(240 \times 15) \div 736 = 4·9$ [German] H.P. for the dynamo or about 6 [German] H.P. for the steam engine; [or $(240 \times 15) \div 746 = 4·8$ H.P. and 5·9 H.P. respectively, calculated according to the British unit]. It should be remembered that a plant of this capacity will require a superficial area of 80 sq. metres [860 sq. ft.], and that with the normal current density of 20 amperes per sq. metre [1·86 amperes per sq. ft.] five months will be required to produce a copper plate 1 cm. thick," [or 6¼ months to deposit a plate ½ in. in thickness].

Although a few among the facts just recorded may now be explained somewhat differently, yet concerning their actual occurrence there is nothing to be altered; and this work remains of permanent value in setting forth the theory and practice of the chemical changes which accompany the electrolytic refining of copper.

The Siemens-Halske Copper Refinery Process.—Meanwhile progress has been constant in the technical application of the process. Even about the year 1870 there were several refineries of various capacities in Germany, and these were soon supplemented by many others. Among the first may be named the experimental installation at the Mansfield Copper Works, the larger plants at the *Norddeutschen Affinerie*, and the *Communion Hüttenwerk* at Oker. But the merit of having brought the electrolytic refining of copper to a high state of development in Germany is especially due to the firm of Siemens & Halske of Berlin. An account will, therefore, be given of their system first, for in many of the later plants the characteristics of the Siemens construction will be recognised at once. A general account of the first copper refinery erected by this firm at Oker, in the Hartz district, was published in 1884, by Fröhlich,* who was the chief electrician to Messrs. Siemens & Halske. He wrote as follows :—"There are at present six dynamos working at this refinery—viz., 5 machines of the C and one of the C_{18} type; and each of these is yielding a deposit of 250 to 300 kgs. [5 to 6 cwts.] of copper daily, with an expenditure of 7 to 8 H.P. The total annual outturn of refined copper amounts, therefore, to 500-600 tons. The copper of which the anodes are cast has already been subjected to a process of refining in a furnace, and contains only 0·3 to 0·5 per cent. of impurities; but in spite of this the electrolytic process is profitable, because the removal of the last traces of

* *Elektrotechnische Zeitschrift*, 1884, p. 466, &c.

impurities enhances the value of the copper very consider-
ably.*

At the Oker Works the two systems of working—with a few
large, or with many small, baths—are in operation side by side,
and have proved themselves equally satisfactory, only for the latter
system the capital outlay is less.   Both the crude and the pure
copper are used in the form of plates about 1 metre long and
0·5 metre wide [39⅜ in. × 19⅝ in.], the thickness of the former
at the beginning of the operation being about 15 mm. [⅜ in.],
whilst that of the latter when sent into the market is a little
less than this.   The machines C_1 are used in connection with a
few large baths, and deposit 250 to 300 kgs. [5 to 6 cwts.] of
copper each *per diem* by a current of 1000 amperes and 3·5 volts.
Each of these C_1-machines operates, as a rule, upon 12 baths
arranged in series, and each of such installations requires a
space of about 80 sq. metres [860 sq. ft.].   The C_{18}-machine gives
a current of 120 amperes × 30 volts (or in other cases a current
of 240 amperes × 15 volts), and is applied to about 80 small
baths in the Oker installation.   The floor space, quantity of the
solution, power, and outturn are practically the same as in
the installation with a C_1-machine.   The cost of the installa-
tion is, however, different, and one of the chief advantages
of the C_{18}-plant, as compared with the other, is that the baths
can be placed at a considerable distance from the machine,
which cannot be the case with C_1."

Fröhlich further says that in the electrolysis of such pure
raw materials, an electromotive force of 0·1 to 0·5 volt might be
used in the baths ; according to the figures quoted above, the
C_1-machine, working with an E.M.F. of 3·2 volts, can be used
with only 12 baths in series, and the C_{18}-machine, working at
30 volts, must be joined up to only 80 baths, and from this the
average E.M.F required per pair of electrodes may be calculated
as about 0·3 volt.   This apparent contradiction is readily
explained by the work of Kiliani† quoted previously, and is
most readily understood by a reference to the table given on
p. 188.

**Limitations to the Industrial Use of the Electrolytic
Refining of Copper.**—The papers written both by Kiliani and
by Fröhlich indicate the great importance of avoiding the use
of a needlessly impure raw material, so that the necessity may
not arise unduly often of replacing an electrolyte that has become
too impure for further use, for this is an operation both costly
and troublesome.   At the same time, by using purer materials,

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* This is no longer (1895) quite in accordance with the market price of
electrolytic copper, since the difference in price between this and ordinary
furnace-refined copper has become considerably less than it was at the time
the above words were written.

† *Berg- und Hüttenmannische Zeitung*, 1885, p. 249.

the application of the current is limited more nearly to the work of transferring copper from anode to cathode. Most refineries, therefore, electrolyse only such refined copper as contains precious metals. It is likely to happen more and more rarely in Europe that black (crude) copper will be bought with a view to refining it electrolytically, either directly or after a previous furnace treatment ; since even the foreign copperworks, from which European refiners have been accustomed to obtain their requirements in the shape of raw copper, have undertaken the work of electrolysis, and are at present applying the process. At the present time, it is only necessary to consider the preparation of the anode copper direct from the reverberatory furnace, which is still commonly used in refining, or from the converter. The process of electrolysis will, therefore, form a sequel to the preliminary work of which a sketch has been given on pp. 173 to 177.

The Siemens-Halske Installation at Goslar.—The following account, with the supplementary illustrations, describes a
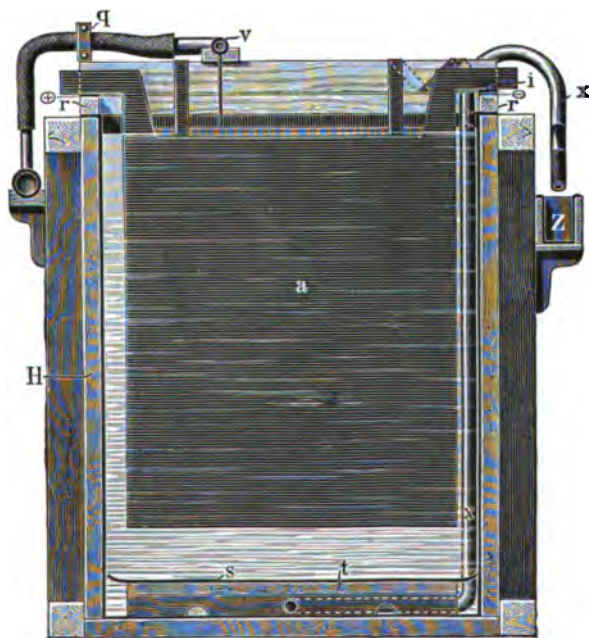
Fig. 88.—Section of copper-refining vat, showing anode (Siemens).

plant erected by Siemens & Halske in the works of Borchers Bros., at Goslar, together with certain noteworthy improvements that have been made by the Messrs. Borchers. The author

acknowledges his thanks to Messrs. K. & H. Borchers, the proprietors of the works, for the information that they have supplied.

The old form of **anode** used in the original Siemens installation has been retained, as shown at *a* in Fig. 88. In the preparation of these anodes, iron moulds or frames, which may easily be put together, or taken apart, are used (Fig. 89.) These frames are laid upon an iron plate, and the copper having been melted, or being ready to tap from the refinery furnace, is ladled or run out, either into stationary moulds placed to receive it, or into others which are caused to travel slowly one after the other in front of the furnace. The **cathodes** always consist of thin copper plate, *k* (Fig. 90).

Fig. 89. — Mould for casting anode plates.

The **baths** or **depositing-cells** are wooden vats (of pitch-pine), H, with a leaden lining, which is bent round over the rims of
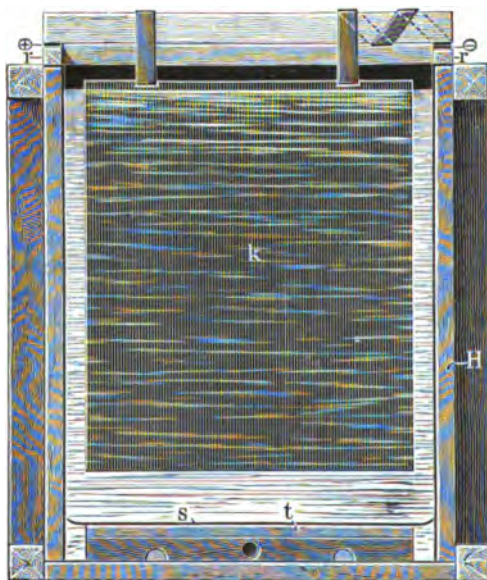
Fig. 90.—Cross-section of copper-vat (Siemens) showing cathode.

the vats. On this is laid the wooden frame, *r*, which is saturated with oil or other suitable substance to prevent it from absorbing water, and which serves to insulate the copper strips, + and —, used as conductors. Before the electrodes are

suspended in place, the lead siphon pipe, x (Figs. 88 and 91), for the withdrawal of the solution, is introduced into the vat; this is followed by the wooden table, t, which rests on the bottom and supports a leaden tray, s; the latter is turned up at its edges, in order that it may collect the deposit of mud which gradually separates from the anode.

The anodes hang directly from the sides of the vat, but must be insulated from the — conductors by the india-rubber plates, i (Fig. 88). The cathodes are suspended by sheet-copper hooks from strips of wood above. One of the copper strips bent
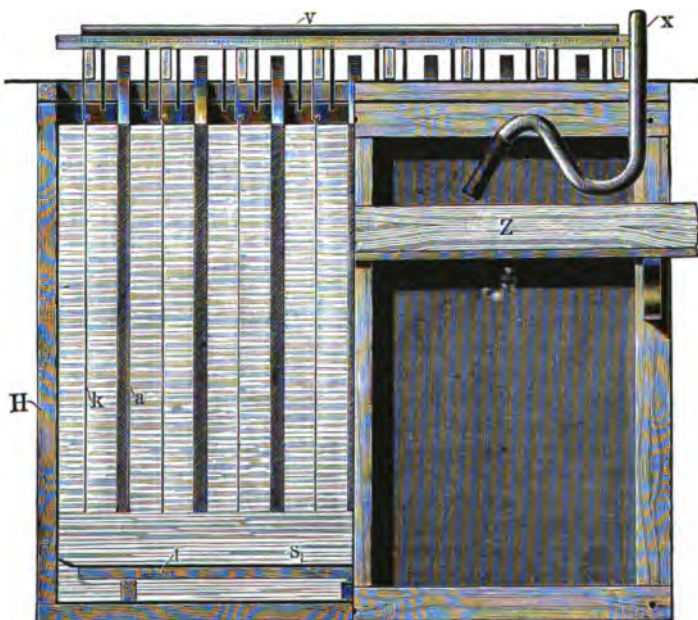
Fig. 91.—Longitudinal section of copper vat (Siemens).

below into a hook, is made longer than the other, so that it may be folded several times around the wood, as shown in (Figs. 88 and 90), and may ultimately make contact with the — conductor, and be in electrical communication with the negative pole of the dynamo.

In order to maintain the circulation of liquid that is so essential to the success of the whole process, every bath is provided with a tube, V (Figs. 88 and 91), to the lower side of which are attached at right angles, a number of narrow tubes, so that the whole arrangement resembles a garden rake. Each of these rakes is in communication, by means of a rubber tube,

with a main pipe, running along the sides of the vats, and conveying the electrolyte solution. The supply of liquid to each rake is controlled by a screw clamp, *q*. The solution is run away from beneath the slime tray through the siphon, *x*, into the channel, *z*.

From Figs. 92, 93, and 94 shown on Plate II., will be seen both the arrangement of the vats and the method of circulating the solution. In order not to detract from the clearness of these illustrations the electric connections of the baths are omitted, but are shown separately in Fig. 95; this figure scarcely requires further explanation. It will be observed that the solution is distributed to the baths from the elevated reservoir, B, and returns through the channel, *z*, to the receivers, C and D. If all of the liquid is to be discharged, or if one of the receivers should leak, the solution is drawn off through a conduit beneath the floor of the room into the tank, E. By means of the pump, P, the circulation of the liquid can either be renewed by transferring it from C, D, or E to the reservoir, B, or, if too impure for further use, it may be removed to the regenerating or cementation plant. Regeneration consists generally in evaporation or crystallisation, if necessary with the aid of chemical precipita-
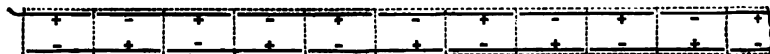
Fig. 95.—Scheme of electrical connections in copper vats (Siemens).

tion. Concerning the cementation process, metallurgical handbooks usually give sufficient information

The points to which special attention must be devoted during the process have been made clear by the work of Kiliani, which has already been described in full. Reference has also been made to the deterioration of the deposit caused by the diminution in the proportion of copper in the bath, which results, under the conditions explained, from an accumulation of non-precipitable metals. So also the importance of maintaining a brisk circulation of the electrolyte, of preserving a certain degree of acidity, and of using a small current density, were sufficiently emphasised by Kiliani.

Borchers' Improvements in the Siemens-Halske Plant.— But the means which, until the last few years, had been commonly employed to fulfil the necessary conditions and to avoid the corresponding sources of failure were quite insufficient. The need of completely renewing the solutions when using the more impure (or even comparatively good) sorts of copper recurred more often than was to be desired in a continuous process; and those who have experienced the trouble of working up such waste liquors would welcome almost any means by which such a labour might be avoided. Many suggestions were, of course,

Fig. 92.—ä
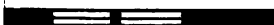
Fig.

made with the object of surmounting the difficulty, and the most natural of these was that a current of air should be forced through the liquors in the vats during the electrolysis, in order to peroxidise the compounds of arsenic, cobalt, nickel, and iron in the bath, and so to induce their precipitation in the vats as arseniates. But the proposal itself was simpler than the method of carrying it into effect. The direct introduction of a blast of air into the solution was satisfactory only for a short time, because it soon led to the production of a turbid liquid, which might almost without exaggeration be compared with chocolate. The hope that this air-treatment would be successful
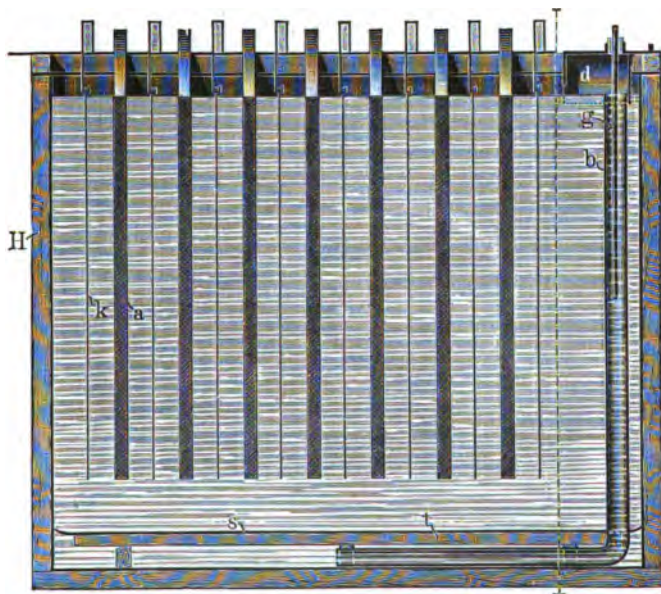
Fig. 96.—Siemens-Borchers' copper vats (longitudinal section).

was therefore doomed to disappointment; and *yet air was clearly the best agent for the purification of the liquors,* if only it could be satisfactorily applied, and the idea of using it must *undoubtedly* be considered *one of the most important discoveries in connection with the refining of copper.* The merit of solving the problem belongs to Messrs. H. and K. Borchers of the above mentioned firm of Borchers Bros.; and this invention, it should be observed, is not patented. The method of carrying it into effect will be first described, and the advantages which it has entailed will be discussed afterwards. A bath fitted with Borchers' apparatus is shown in Figs. 96 and 97. On comparing these with the

previous figures, it will be seen that there has been practically no change in the arrangement of the electrodes. But there has been added a wide leaden pipe, *b*, which passes downwards from the upper surface of the liquid to the very centre of the space beneath the mud-depositing tray, *s*; and within this pipe is a glass tube, *g*, drawn out to a fine jet at its lower extremity. The glass tube is passed through a stopper in the leaden cap, *d*, by which the tube, *b*, is surmounted, and is so arranged that it

Fig. 97.—Siemens-Borchers' copper vats (cross-section).

may easily be raised or lowered in position. A current of air is continuously forced through the glass tube into the column of liquid in the pipe, *b*, with the result that the air, dividing itself into small bubbles as it rises to the surface, lowers the specific gravity of the contents of the tube, *b*, and causes a portion of the liquid to overflow into the vat, where it mixes with the bulk of the electrolyte. Meanwhile, solution from the lowest level of the bath is constantly entering at the bottom of the tube, *b*. The aëration of the electrolyte is thus effected very

Room for Measuring Instruments.
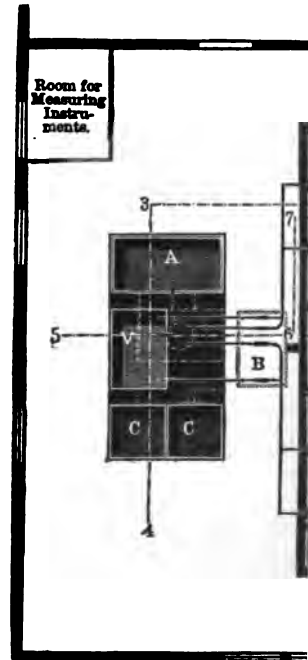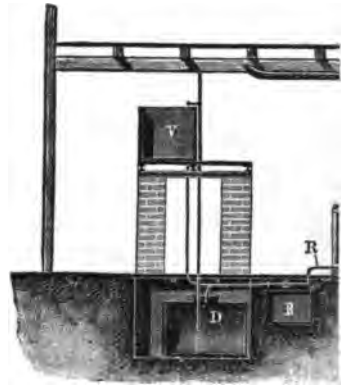
To face p. 197.]

quietly and uniformly, whilst at the same time the method of applying the air affords the most practical and economical means of circulating the liquid. The process would therefore commend itself to the notice of the refiner on the latter ground alone, even if we disregard the advantages to be derived from the chemical action of the air, which, however, must not be underrated.*

A glance at Figs. 96 and 97, suffices to show that a very inconvenient portion of the older apparatus—the "rake" for distributing the solution—has been dispensed with, and that the side channels for the conveyance of the liquid have also disappeared. These two attachments of the original installation had rendered cleanliness in working the process impossible, owing to the constant and unavoidable splashing of the solution; while at the same time they prevented ready access to the electrodes, and were, in fact, the chief sources of trouble in the whole installation on account of the constant supervision that they demanded.

Details of the Siemens-Borchers' Installation.—In the plant, as at present used, both the filling and discharging of the baths are effected by a single pipe, R (Fig. 96, and Plate III., Figs. 98, 99, 100), the former being done once for all at the beginning of a refining operation, and the latter being necessary only when the impure liquors have to be run off at the end, or as required. This is in striking contrast to the older system, which necessitated a constant circulation of the electrolyte through the whole series of vats. Every individual vat is connected with the main pipe, R, by means of a siphon, N, attached to it by a rubber tube, S. During the working of the process this tube, S, is closed by a screw clamp, so that there may be no electrical communication between the baths.

Plate III., like the previous plate, is concerned mainly with the method of circulating the solution, and with the general arrangement of the electrolytic plant, the details of bath construction having been shown on a larger scale in Figs. 96 and 97. In the new installation a compressed air-chamber, D, effects the conveyance of the bath-liquor. In starting work the electrolyte, placed originally in A, is allowed to run into the pressure vessel, D, whence it is forced into the distributing vat, V, so that it may flow to the vats through the pipes, R, and the siphons, N. The liquid may be discharged from any given vat during the electrolysis by drawing it into the pressure chamber, D, through the

* [According to the *Engineering and Mining Journal*, 1896, vol. lxii., p. 603, it is found desirable, in practice, to assist the circulation of the electrolyte for two to three hours in the course of a day, by causing a general circulation from vat to vat, in addition to the air-mixing accomplished by Borchers' device. The same authority disputes the statement that arsenic is precipitated (see p. 195) and eliminated in this process.—TRANSLATOR.]

siphons, N, and the mains, R, so that it may be treated either for the recovery of its salts or by cementation or regeneration. Any solution which may escape in consequence of leakages in the vessels or conveying pipes, or through irregularities in the working of the vats, is conducted through the drains, G (placed beneath the flooring), into the tank, B, whence it may be conducted to the pressure chamber for re-distribution. The vats, C, for the washing of the anode slimes have also found a place in this room under the present arrangement.

Among the other advantages of this process one of the most remarkable is the comparatively lasting purity of the electrolyte solutions. The behaviour in the tanks of the iron, arsenic, and other substances originally present in the anodes was explained by Kiliani. By the introduction of the air these two materials are precipitated together in the form of ferric arseniate, even in acid solutions; and this result is obtained so quietly that the liquors *remain perfectly clear;* this freedom from turbidity is an advantage that cannot well be over-estimated, when search has to be made for the faults in electrical conductivity that sometimes occur. Bismuth and antimony compounds are also precipitated if the acidity of the bath be diminished, and then in part remain undissolved in the slime that is deposited. It is evident from the above that the new modifications of the process must reduce the frequency of running off, and regenerating, or otherwise working up, the vat liquors; and in the absence of antimony and bismuth from the anode copper these troublesome operations may almost be dispensed with. Siemens and Halske recommend that the solutions should be warmed, the conditions being then more favourable to the precipitation of antimony and bismuth compounds.

Purification of Old Liquors from Bismuth and Antimony.—If, in course of long use, the electrolyte should become saturated with compounds of these two metals, it must be run out of the vats into a specially prepared tank, and be there warmed, treated with air forced through it by means of a steam injector, neutralised with copper oxide or other suitable basic copper compound that may be at hand, and filtered. After reserving a portion of the solution so obtained for working up into copper sulphate, the remainder is returned for use in the refinery, after adding sufficient sulphuric acid, and bringing it to the normal strength, for the work.

Reduction in the Cost of Electrolytic Refining.— Finally, a by no means unimportant gain in using the new process, is to be found in the fact that the current density may be increased from 30 to 100 amperes per sq. metre [9·3 amperes per sq. ft.] without detriment to the texture or surface of the deposited copper. The full meaning of this advantage will be appreciated after a perusal of the following translation of a

private communication from the firm of Siemens & Halske to the author :—

"The possibility of considerably increasing the current density has the great advantage that, for the same outturn of refined copper, the floor space occupied by the baths, and the quantity of copper, silver, and solution locked up in the vats, will be reduced to about one-third, and the item of wages will be considerably lower. On the other hand, the power required will be greater; in spite of that, however, there will be a considerable nett saving in the working cost. In the following table the estimated cost of working at 30 amperes and 100 amperes per sq. metre are placed side by side for comparison, the calculation being based upon the ordinary conditions of work in Germany. Where other conditions prevail, the necessary alteration in the figures may readily be made; but in any case the difference between the costs of working by the old and new processes will remain very much the same as is here indicated :—

COMPARATIVE WORKING COST WITH HIGH AND LOW
CURRENT DENSITY.

Daily working cost for an output of 1 ton of refined copper per diem.	Former current density 30 amps. per sq. m.	Present current density 100 amps. per sq. m.
Cost of power (1 H.P. hour = 5 pf.), .	M. 17	M. 30
Wages, ...	30	15
Interest on copper locked up (5 %), .	15·60	4·80
Amortisation of the electric plant (10%), .	8·30	4·15
Cost of heating the baths, 250 kgs. [5 cwts.] coal, ...	...	5
Cost of regenerating the electrolyte, .	4	...
	74·90	58·95

"From this table it is evident that the actual cost of refining has been reduced by about 20 per cent. through the introduction of the new process; and since the interest, both on the capital sunk in buildings and site, and on the silver in the anode copper, will also be reduced, the actual comparison is even more in favour of the application of high current density than would appear from the above table.

"In order to introduce the improved process into existing works, either the present baths, after the necessary alterations have been made in them, may be used to produce a higher output of copper by increasing the power of the engine and dynamos; or the same power may be employed with a smaller electrolysing plant and a somewhat diminished outturn, but with a higher efficiency; in the latter case, about three-quarters

of the area originally occupied by the baths will be set free, and so rendered available for other purposes. Generally, however, the former alternative will prove more advantageous."

The method of work and the construction of the apparatus above described undoubtedly possess all the advantages which may reasonably be expected from a well-planned electrolytic installation—namely, simplicity of arrangement, convenience of access, and control in all parts, cleanliness in operation, and exclusion as far as possible of all intermediate work of a disturbing character. It might have sufficed to limit the account of copper refining to that already given, and to recommend the system of Siemens-Borchers for universal application, but within the last few years certain other processes have been most highly spoken of in prominent metallurgical journals. They are, however, more or less deficient in originality and in the advantages above referred to, and a few of them only will therefore be described in brief.

[Before proceeding to the consideration of these processes, however, it may be worth noting that in American practice a much higher current density is used than that employed in Europe : it is rarely much lower than 10 amperes per sq. ft., and, in some cases, is nearly double that amount. In consequence of this the turnover is greater, and the cost of refining is correspondingly reduced, inasmuch as the fixed charges are distributed over a much higher tonnage of refined material, and the interest on capital locked up in the copper in the vats is also diminished. The whole process is worked at a lower cost, and this helps to compensate for the higher charge for wages. Thus, although the average wage at the Anaconda Works (see p. 202) is about $3 per diem, the cost of refining (including that of treating the silver mud) is only $14 (£2, 18s.) per ton, whilst at Perth Amboy (New Jersey) it is stated (exclusive of office expenses) to be $9 (£1, 17s.) per ton, as against 59 marks (£2, 19s.) per ton in the table given on p. 199. The charge for labour at Perth Amboy is less than half that at the Anaconda Works, but it is still nearly double that in Germany. Hence the gain in applying the highest current density that can be safely used, without endangering the quality of the deposited copper, is emphasised as strongly as by the figures quoted in the above table (*loc. cit.*).—TRANSLATOR.]

[Schneider and Szontagh System.—A system of air circulation, similar to that of Borchers, has been patented in the United States by Schneider and Szontagh.* The method of introducing the air into a vertical pipe communicating with the electrolyte tank above and below is practically the same; but, instead of taking off the liquid from beneath the centre of a tray, it draws it through perforations in a horizontal pipe running

* [U.S.A. Patent 563,093, June 30, 1896.]

along the whole length of the vat at one of the bottom angles, whilst the solution overflowing from the upright air-pipe passes through a second horizontal pipe, which is placed along the top of the vat on the opposite side. From this pipe it is delivered into the tank through perforations pierced between each pair of electrodes, and increasing in diameter as they are further removed from the vertical pipe, in order to secure a greater uniformity of flow. The system is in use in the large refinery of Messrs. Guggenheim at Perth Amboy, New Jersey.—Trans-lator.]

The Thofehrn Process.—According to the account of this process published by Hering,* it may be distinguished from all others by the use of very *large baths*, for which either wood lined with lead or concrete painted with tar may be employed. The baths have a width of about 2 metres, a length of 3 metres, and a depth of about 1·5 metres [6½ ft. × 10 ft. × 5 ft.]. The form of the anodes is the same as that adopted in the Moebius appar-atus for treating silver,† and the method of suspending them in the bath is also the same—viz., by hanging several small plates from a metal bar. In Thofehrn's baths each anode rod carries
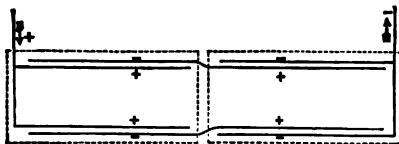
Fig. 101.—The electrical connections of Thofehrn's apparatus.

three plates 0·6 metre long by 0·6 metre wide by 0·02 metre thick [2 ft. × 2 ft. × ¾ in.]. The cathode consists of copper plates, of which six are hung on every rail, each one being 0·6 metre long by 0·2 metre wide by 0·0002 metre thick [2 ft. × 8 in. × 0·008 in.]. A diagrammatic sketch of the position of the conductors used in conveying the current to the supporting rods for the electrodes is given in Fig. 101. It will be recognised at once as an old arrangement which was described in metallurgical text-books ‡ long before any account of Thofehrn's process was published. As an electrolyte for black copper anodes with a current density of 30 amperes per sq. metre [2·8 amperes per sq. ft.] he recommends an aqueous solution of 15 per cent. of copper sulphate and 5 per cent. of sulphuric acid; or with 50 amperes per sq. metre [4·6 amperes per sq. ft.], one of 20 per cent. of copper sulphate and 5·5 per cent. of sulphuric acid; whilst for bessemerised copper and a current of 60 amperes per sq. metre

* Hering, *Berg- und Hüttenmännische Zeitung*, 1893, vol. lii., p. 53; from *Revue Industrielle*, 1892, p. 24.
† See Chapter on *Silver*.
‡ C. Schnabel, *Handbuch der Metallhüttenkunde*, vol. i., 1894.

[5·6 amperes per sq. ft.] he prefers a bath containing 25 per cent. of the copper salt and 6 per cent. of the acid.   The circulation of the solution from bath to bath is effected with the aid of siphons, which, however, afford no security for the uniform circulation of the electrolyte through the large baths themselves.   The author, therefore, considers it unnecessary to enter into a discussion of the full details of the Thofehrn system.   All the details of the process and apparatus have been employed by other inventors, and some have been given up again as unpractical.   Those whose attention may have been directed to this process by the accounts published in the technical journals, and who are sufficiently interested in the matter, will find full particulars given by Hering (*loc. cit.*).   The chief recommendatory feature described in the account of the Thofehrn plant is the method of suspending the anodes, and this idea was borrowed from Moebius, as noted above.   [But see next paragraph].

[**The Anaconda Copper Company's Installation under the Thofehrn System.**—The Anaconda Copper Company who, a few years since, used the Hayden series process (see p. 209), have recently completed an installation of the Thofehrn system, capable of producing 150 tons of refined copper per diem.   A description of this colossal plant was published in 1896,* and is especially interesting as an account of the arrangements successfully adopted for work on an unusually large scale in a district in which both fuel and labour are costly.

The current is generated by four 270 kilowatt Westinghouse generators, directly coupled to two triple-expansion engines of 900 H.P. each, together with one of the same type and size, belt-driven from a double Corliss engine of about 800 H.P.   In addition to these, a 220 K.W. generator is held in reserve, to be belt-driven from a 400 H.P. Westinghouse compound engine, and to be switched on to any of the circuits in the refinery at will, in case of a breakdown.   The boiler capacity is said to be 62,200 lbs. of water evaporated per hour, of which the two triple-expansion engines use 23,160 lbs. (equivalent to 1544 H.P. at 15 lbs. per H.P. per hour) in generating 1080 kilowatts of electricity, while the Corliss engine requires 22,500 lbs. of water per hour (750 H.P. at 30 lbs. per H.P. per hour—but 50 H.P. of this is lost in the belt-transmission of power) to produce 490 kilowatts.   Besides this, however, 1500 lbs. of steam (50 H.P.) are used hourly in running the electric lighting and power plant, and 900 lbs. (30 H.P.) in working the acid pumps, whilst finally 1500 lbs. are required for heating, and a like amount for the condensers of the engines.   This expense of power is sufficient for the production of 150 tons of copper per day of 24 hours. It is considered that the total power required to refine the copper by this plant, including the cost of handling (by electrical

* *Engineering and Mining Journal*, 1896, vol. lxii., p. 271.

plant), making the cathodes, operating the silver-mill, and lighting the whole installation, amounts to 17½ H.P. hours per ton.

The vats are systematically arranged in two large buildings of corrugated iron, supported upon wooden framework, each building covering an area of 6500 sq. yds., and containing 600 electrolytic tanks. Every tank is 8 ft. 3 in. long by 4 ft. 7 in. wide, by 3 ft. 3 in. deep. They are made by constructing a wooden frame in the shape of a regular girder, and lining it with common planks, and dividing it up by wooden partitions into ten tanks of the above size. The joints of the wood are well caulked with an insulating material, and each tank is lined with lead, care being taken that the lining shall be protected from contact with the copper electrodes, which would cause a galvanic action, the lead being the metal attacked. These groups of tanks are so built that they are exposed to the air on all sides, and access may readily be had to all parts, including the bottom. Copper rods, connected with the positive and negative leads from the dynamo, run at two different levels along the top rim of the vats, and on these are supported respectively two sets of iron bars, which rest transversely across the bath, and carry the electrodes by means of stout copper hooks. The actual number, size, and disposition of the electrodes are not stated, but from the illustrations given it would appear that to every vat there are 16 cathode rods, and 15 anode rods, each supporting two or more strip-electrodes. There are thus 10 vats placed end to end in a row, and there are ten rows placed parallel to one another with gangways between; the 100 vats form a set or block at one end of the room, whilst a similar set is arranged in the other half of the floor; so that in one "hall" there is a complete system of 200 vats; this system is operated quite independently of the other sets which are placed in different halls. The electrodes in each individual tank are placed parallel to one another, but the 200 tanks that form one system are coupled in series; in effecting this the copper conducting rod along the margin of the first vat is extended along the rim of the second tank, but has a bayonet bend between the two, so that it forms the anode rod of the second tank at a different level; similarly the cathode rod of this latter vessel is bent and extended to form the anode connection for the third tank, and so forth. The necessity for the use of binding screws is thus dispensed with, and no trouble is experienced from bad electrical contacts caused by the corrosion of connecting clamps. The rows are built on an inclined plane, and the circulation of the electrolyte from vat to vat in each row is ensured by gravity, the liquid from the last tank being taken to a collector, whence (after undergoing a partial purifying process not described) it is re-distributed by acid pumps, worked

Fig. 101A.—The Anaconda Thofehrn installation.

by air-pressure. Electric overhead travelling-cranes command the whole of the floor, and may be brought into operation in connection with any tank at will. Electric tramways of 20 in. gauge are brought on to the working floor of each hall, and other similar tramways run beneath the tanks. Fig. 101A shows a general view of one of the electrolytic tank rooms at the Anaconda works.

In practice, the blister copper, containing generally about 98 per cent. of copper, together with arsenic, antimony, iron, lead, tellurium, selenium, and about 110 oz. of silver and $\frac{1}{3}$ oz. of gold per ton, is cast into the form of anodes. The anodes are conveyed in the electric tramway to the depositing rooms; here they are arranged in a frame and conveyed by the electric crane to the vat for which they are intended. Meanwhile, this tank will have been cut out of the electric circuit, and out of the flow of the liquid, both the current and the circulation being continued without interruption through the remaining tanks); the cathodes, with their charge of electrolyte copper and the remnants of the anodes, will have been lifted out by the crane and carried to the tramway; and the slimes, or "silver mud," will have been washed out into lead-lined cars beneath the tanks, to be transported to the silver refinery. The vats are then refilled with solution; the crane brings up first the frame of anodes, which are lowered into the exact position required, and then a similar frame of cathodes, which are treated in the same way; and finally the tank is included in the electric circuit. The whole operation of discharging and re-charging one tank should occupy scarcely more than one hour.

The system of checking the progress of the work is especially worthy of mention. Each series of five tanks is connected up to a kind of dynamo commutator, in such a way that the opposite poles of the same series of five vats are joined up to radial copper plates at the opposite ends of one diameter of the commutator. These plates are all insulated from one another. A yoke-piece with two brushes, diametrically opposite, is revolved around the commutator once an hour; and the brushes are connected to an automatically-registering voltmeter, so that each series of 5 vats is individually connected up to the latter instrument, and the slope of potential between the terminals of each of these series is therefore registered serially once every hour. The manager is thus able to detect and to locate precisely any irregularities that may be taking place.

There are 120 men employed in the works, including the foreman, assayers, and clerks. In the depositing houses there are 75 men, of whom 50 are engaged in the older building, whilst only 25 are required for the same outturn of copper, in the new building, owing to the perfection of the labour-saving appliances

used. The average wage is $3 per man per diem, and the cost of fuel is $5.50 per ton; but the latter will shortly be reduced to $2 per ton. About 100 tons of copper are at present being treated per diem, half in each building; and the cost of refining, including that of treating the silver mud by chemical processes, amounts to $14 (£2, 18s.) per ton of refined metal.

Neither the current density employed, nor the E.M.F. required for each pair of electrodes is given; all that is stated on this subject is that in Thofehrn's refineries the current density generally used is 10 to 20 amperes per sq. ft. The copper produced is melted into ingots or wire bars at the cost of about $4 per ton; and this metal, in the form of hard drawn wire, containing, as it must at least, a trace of cuprous oxide, is found to have an electrical conductivity of 98 (Matthiessen's standard), and a tensile strength of 64,000 to 65,000 lbs. per sq. in.; the number of twists obtainable in 6 in. of No. 12 wire is 80; elongation, $1\frac{1}{4}$ per cent.—TRANSLATOR].

Thofehrn's New Process.—The same number of the *Engineering and Mining Journal (loc. cit.)* describes a new process in which the copper is deposited upon a long hollow cylindrical cathode 8 ft. long and 3 ft. in diameter, which is immersed in the electrolyte, and is revolved at a low speed, whilst the copper is deposited upon it with a current density of 50 to 100 amperes per sq. ft. During the time of depositing, numerous jets of the electrolyte solution are caused to play under pressure upon the surface of the cylinder.* It is stated that the crystals of copper are deposited in the form of microscopic octagonal hair-like filaments, which become felted and compressed by the jets of liquid; and that the cylinders of copper when they have been deposited an inch thick and have been detached from the cathode cylinders may be rolled direct. It is said that the wires are over 15 per cent. stronger than those prepared by the old electrolytic refining process followed by fusion; and that the expense of such an electric refining of the metal to produce

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* [A similar device has been adopted by Graham (English patent 986, Jan. 14, 1896. According to his specification, a nearly saturated solution of copper sulphate, containing 5 ozs. of strong sulphuric acid per cb. ft. of water is used as electrolyte, and is stored in reservoirs placed at a height of from 1 to 2 ft. above the electrolytic tanks, thence it is conveyed to $\frac{3}{4}$-in. jets that deliver it in a stream upon the surface of the cathodes, which are placed at a distance of $1\frac{1}{2}$ in. from the orifices of the jets. It is stated that a current of 300 amperes per sq. ft. may be employed with safety at all points within the sphere of influence of the jets; beyond this area, it is obvious that the deposit would be pulverulent and useless. The radius of the protected area is found to be 5 ins., and the number and disposition of jets employed must be arranged accordingly. The anode should have a surface area eight or nine times greater than that of the cathode, and its shape should preferably be that of a corrugated spiral or of a grid, through which the electrolyte streams are directed upon the cathodes. The edges of the latter are protected by an insulating material.—TRANSLATOR.]

the bars required for the rolling or wire-drawing mill is $16 (£3, 6s.) per ton.

One distinct advantage in the use of these jets is obviously to be found in the certainty that the electrolyte at the surface of the cathode is constantly and thoroughly renewed, so that a very much greater current density may be employed than would otherwise be possible. No details whatever are given concerning the process, and it is therefore premature to criticise it. It may be noted that the same paper states that white metal anodes with 75 to 80 per cent. of copper have been employed in this process with success, but no hint is given as to the manner in which difficulties that have baffled the attempts of previous inventors have been obviated.—TRANSLATOR.]

Modified System of Deposition.—It need hardly be pointed out that many other modifications of the plant originally described have been made, and have received titles, suggestive of the credit due to those who made the new "discovery," or "improvement." Reference to the names of the original inventors is usually omitted.

The Stalmann Process.—The original voltaic battery has been made the foundation of another system of arranging electrodes, which has come into use in various modifications, and in some cases with the stated object of economising cathode plates. Schnabel* describes one of these methods (in which, however, special separate cathode plates are used), and states that he has seen it in use in the Anaconda Works at Montana, U.S.A. Without this testimony it would have been very difficult to believe that this most inconvenient arrangement should have found any favour in practical work; but as it has been shown to be possible, it will be necessary to describe the apparatus and the method shortly at this point, the account being taken from the patent specifications of Stalmann† whose process it is.

Stalmann couples the electrodes of each individual bath in series, suspending an anode first, and then cathodes and anodes alternately, united in pairs, until at last a cathode plate ends the whole series. The first anode and the last cathode are connected immediately with the main leads of the circuit, or are joined up in series with other baths similarly arranged. The details of the electrode connections in the bath are shown in Figs. 102 to 105. In arranging the first pair of electrodes, either the cathode plate, k, is fastened directly to the anode, a (Fig. 102), or each anode plate, a, is connected with a cathode plate, k, by means of a wire or by the short copper bars, v, lying on the rim of the vat (Fig. 103), or, finally, the anode, a, is united to the cathode, k, in the manner shown in Fig. 104, with

* C. Schnabel, *Handbuch der Metallhüttenkünde*, vol. i., p. 270 (1894).
† U.S.A. Patents 467,350 and 467,848, Jan. 19, 1892.
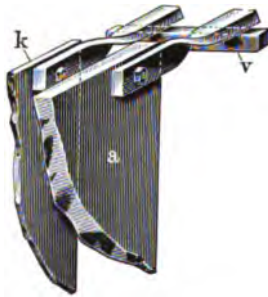
Fig. 102.   Fig. 103.   Fig. 104.
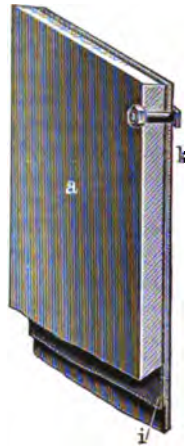
Stalmann's electrode connections.
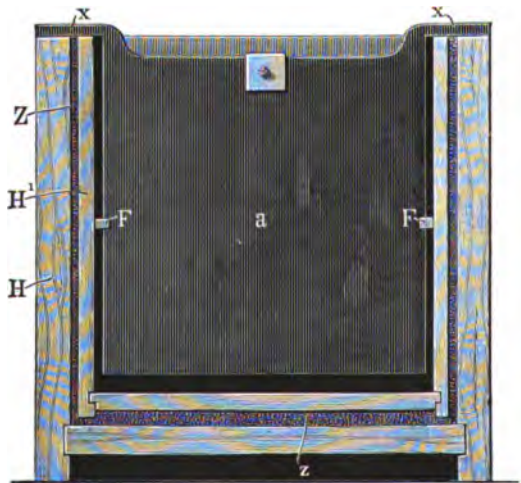
Fig. 105.—Stalmann's copper vat (cross section).
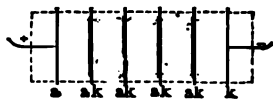
Fig. 106.—Scheme of electrical connections in Stalmann's vat.

a plate, i, of insulating material separating them, so that only one side of each plate comes in contact with the solution.. The last-named method is the latest. The pairs of electrodes are suspended in the baths after the fashion adopted in the older systems. If the electrodes are not attached by screws to supporting arms as shown in Fig. 103, the anode plates, a, are cast with projecting lugs, x (Fig. 105), by which they are supported on the rim of the bath. The electrolyte vats (H and H¹) are double, one being placed within the other, whilst the intervening space is filled up with paraffin wax, tar, or other similar material; they are made of wood, and the inner vessel is provided internally with a series of wooden studs, F, on its side walls to prevent any displacement of the electrodes. The connections of the electrodes and conductors will be understood on reference to Fig. 106, in which a is the first anode, k the last cathode, and ak the intermediate double electrodes. It is not easy to understand from this patent specification what advantages Stalmann's arrangement possesses over the other systems in use.

The Hayden, Smith, and Randolf Processes.—Hayden* simplifies this apparatus by omitting all the cathode plates except the one connected to the negative wire of the generator. He joins up the first anode plate to the positive lead from the dynamo, and suspends behind it a series of crude copper plates insulated from it, and from one another, and finally connects a plate of pure copper to the negative lead. The pure copper is therefore deposited on those sides of the intermediate plates that are turned towards the first anode, whilst the metal is at the same time dissolved from the other sides, which face towards the last negative plate. But, unfortunately, the crude copper plates, which are always of cast copper, are never quite uniform in structure; or, even if the electrodes could be obtained perfectly homogeneous, certain irregularities, due to the clinging of the insoluble residue to the surface and the like, would be unavoidable; there must, therefore, be a more rapid solution of the metal at some places than at others. Cavities are thus formed, which, in course of time, extend to the pure metal deposited (by this time to some thickness) on the other surface; and it goes without saying that the pure copper must then be dissolved. Fig. 107 shows the electrical connections in the Hayden bath in which a is the anode, and k the cathode plate. The intermediate plates, z, serve as cathodes on their left-hand, and anodes on their right-h and surfaces.

[The Hayden process, which was introduced in 1886, may perhaps
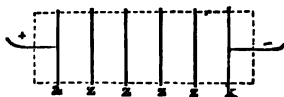
Fig. 107.—Scheme of electrical connections in Hayden's vat.

* *Engineering and Mining Journal* (New York), 1892, vol. liv., p. 126.

be said to have been anticipated in principle by Hugon in 1884 and by Farmer* in 1885. The Hayden system was at one time very largely employed in America, and although in most cases it has been relinquished, it is still used in the large works of the Baltimore Electrical Refining Co. It is said, however, that even here a large quantity of scrap copper is produced in working it; and this is of necessity a serious disadvantage. Difficulty is often found in series processes in stripping the deposited copper from the residue of the previous anode material; the labour involved in this process adds considerably to the cost of refining; and occasionally it has even been found more economical to remelt the whole cathode with the next charge of anode metal. To obviate this, Stalmann has proposed sticking a sheet of paper to the back of each anode, fastening a few rivets through, and black-leading the surface of the paper. By this arrangement the copper would be deposited upon the paper instead of upon the surface of the anode copper. —Translator.]

If Fig. 107 be turned through a right angle, so that *a* is placed at the top and *k* at the bottom of the illustration, and if canvas diaphragms be imagined stretched between the electrodes, a fair mental picture of the Smith system† will be obtained. The object of the canvas diaphragms is to retain the deposit of anode mud, which would otherwise fall upon the surface of the cathode below and render the deposited metal impure.

If now the same figure be turned in the opposite direction, so that *k* is at the top and *a* underneath, the principle of the Randolf arrangement‡ is sufficiently clear. The copper irons in this case travel upwards, and as the impurities, therefore, remain beneath, there is no need for the diaphragm which was employed by Smith. The circulation of the solution is effected in a horizontal direction.

In both these latter forms of construction, the discovery of the cause of any accidental disturbance of the operation is rendered much more difficult. With the vertical suspension of the electrodes, however, such a disturbance is readily found, and very often is easily remedied. Neither of these methods, therefore, appears to afford any grounds on which its adoption could be recommended.

[The Multiple and the Series Systems of Refining.—The usual processes of copper refining, such as those of Siemens-Halske, Thofehrn, and others, in which all the anodes in any one tank are hung in parallel circuits, are now classed as belonging to the Multiple system, to distinguish them from the Hayden and similar processes, in which the anode and cathode

* [U.S.A. Patent 322,170, July 14, 1885.]
† *Engineering and Mining Journal*, 1892, vol. liv., p. 126.
‡ U.S.A. Patent 514,275, Feb. 6, 1894.

pairs within the vat are connected in electrical series. The latter arrangement is accordingly known as the Series system. It must be remembered that these terms refer only to the disposition of the electrodes in a single tank, and do not in any way relate to the connections of the different tanks in the installation, which must be so grouped in a combination of series and parallel, as to give the maximum economy with the current conditions available, taking into account the interest upon the capital locked up in the copper contained in the baths, as well as in the plant itself. The selection of the above-mentioned names is, therefore, somewhat unfortunate, as it tends to confusion. The amount of copper deposited under the multiple system should not be less than 95 per cent. of that which is theoretically possible, whilst in the Series processes a higher E.M.F. is required for each tank, and there is a greater loss by short circuiting through the mud upon the bottom of the bath and through the walls of the tank itself, so that the electrical efficiency is reduced to from 85 to 90 per cent. The capital represented by the copper electrodes is also greater in the case of the Series system than in the Multiple; but, on the other hand, the total capital expenditure is higher in the latter case. Kroupa states that, weighing the costs of the two processes one against the other, the balance in favour of the Multiple system works out at about 8s. 4d. per ton of copper, a difference which is quite sufficient to account for the substitution of this system for the series in so many of the works in which the latter had been tried.—TRANSLATOR.]

Refining of Argentiferous Copper.—In addition to the argentiferous blister or refined copper which results from the smelting of copper ores, alloys containing little copper but much precious metal often come to gold and silver refineries for treatment. But as, in most instances, it is found necessary to bring the silver into solution when electrolytic processes are applied, the method of treating these alloys will be referred to in the Chapter on *Silver*.

Treatment of Sulphide Ores and Mattes.—This problem is more difficult than that of electrolytic refining, and, indeed, it cannot as yet be regarded as solved. For a long time the obstacle to the solution of the problem consisted in the fact that those who took the matter in hand allowed themselves to be led away into following the objects aimed at in electrolytic refining. Thus they attempted the utilisation of all the arrangements that were known to be available in refining, as types for the treatment of an anode material that required an altogether different method of handling. Both the composition of the anodes and the residue that was left after electrolysis, were different from those to which metallurgists were accustomed in the treatment of metallic anodes.

It has been shown that in the preparation of anodes for electrolytic copper refining a metal is commonly used in which the impurities amount to only a fraction of 1 per cent. of the total metal present; and it must be remembered that these impurities consist largely of metals, which do not take part in the chemical reactions of the process, and which are not chemically combined with the copper, but only alloyed with or simply dissolved in it. Then, after electrolysis has commenced, the copper is gradually and more or less uniformly removed from the surface of the anode, whilst a slight insoluble residue is at first left in its place. This residue, consisting for the most part of the precious metals, lead peroxide, cuprous oxide, and the like, is very small as compared with the weight of the copper in which it was dissolved, so that it separates in a non-coherent form, and, becoming detached very soon from the metal plate, collects (on account of its high specific gravity) as an anode-mud at the bottom of the bath. Hence the anode surface remains comparatively clean, and the small quantities of impurity which cling to it for a short time, offer scarcely any hindrance to the progress of the work; they are for the most part conductors.

But these are conditions of so exceptionally favourable a kind that they are but rarely met with in the whole course of metallurgical practice. It is true that an alterable material has to be dealt with in the treatment of anodes prepared from ores or mattes, for the sulphides of which the anodes are formed are decomposed by the current in such a manner that the metal, leaving the sulphur behind, passes into the electrolyte, and, so far as it is capable of precipitation under the conditions obtaining, it is deposited upon the cathode. The reactions by which this is brought about may be left for future consideration. It is well known that in ores and mattes copper is not the only soluble metal to be dealt with, and Kiliani has shown, further (see p. 183-189), how important it is for continuous work that as few foreign substances as possible should pass with the copper into the electrolyte. This is clearly an argument against adopting the method of treatment which is possible in the case of copper refining. It may here be remarked that it is sometimes desirable to make test-experiments on a large scale, even in the face of unfavourable prospects. But in this instance, costly installations have often been almost recklessly erected, with the object of investigating disagreeable truths that might have been discovered at a much less expense. A continuous experiment with one, or at least with quite a few, baths of the same dimensions as would have been used on a large scale and requiring only about 2 to 3 H.P. would have sufficed to show all the difficulties connected with this method of work. And these difficulties are very numerous and serious.

The Marchese Process.—The *Società anonima Italiana di*

Miniere di Rame e di Elettrometallurgia in Genoa has, at a great sacrifice, obtained proof of the impracticability of this method of treating copper mattes; for they erected a plant of some 125 H.P. at their works at Casarza in order to put the process of Marchese* to a practical test. According to the account given by Badiat the work and the installation at this place were as follows:—

The smelting of the coarse-metal (matte), of which the anodes were made, was accomplished in the usual way; and, at first, a matte containing 30 per cent. of copper, 30 per cent. of sulphur,

Fig. 109.

Fig. 108.
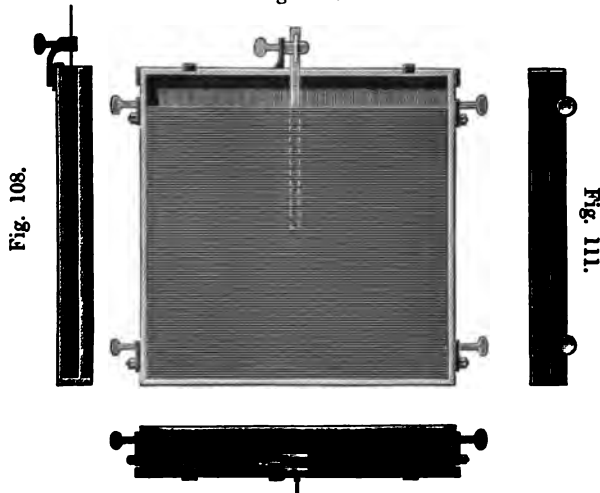
Fig. 111.

Fig. 110.

Moulds for casting anodes of matte at Casarza.

and 40 per cent. of iron was considered sufficiently good. The moulds used in casting the anodes are shown in Figs. 108 to 111, which need no further description. The anodes measured 800 × 800 × 30 mm. [31½ × 31½ × 1¼ in.]. Each mould was provided with a clamp, which served to hold in its place a copper strip that was to be inserted in the anode. This strip was used subsequently for making the necessary electrical connection with the dynamo during electrolysis. It may here be pointed out that, according to a later proposal of Stolp's,‡ a copper wire net should be cast into the block of matte, in order, on the one hand,

* German Patent 22,249, May 2, 1882. [English Patent 1884, 1882.]
† *La Lumière Electrique*, 1884, vol. xiv., Nos. 40, 42, 44.
‡ *Engineering and Mining Journal*, New York, 1886.

to give more stability to the anode plate which is very easily ruptured, and, on the other hand, to ensure a more uniform distribution of the current to the sulphides.   But even this proposal has not been able to save the Marchese process.   The plates must be very slowly cooled after casting; for this reason the moulds were surrounded with some material that is a bad
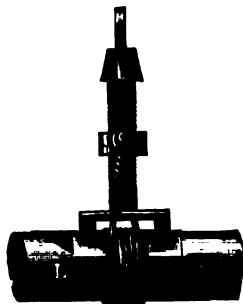
Fig. 112.   Fig. 113.

Connections of anode-strip with main conductor at Casarza.

conductor of heat, and they stood during the casting and cooling operations in pits sunk in the floor of the melting-room.   It was not, of course, proposed to suspend plates of such weak and brittle material by the copper plates inserted in them.   They were to be placed upon a wooden support provided for them in the baths.   The copper strips were, however, bent around strips of wood in the same way as those which were also used for suspension (compare Fig. 90), and were then fastened to the conductors, which lay along the sides of the vat, in the manner indicated in Figs. 112 and 113.
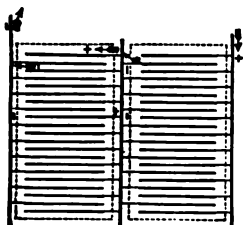
Fig. 114.—Scheme of electrical connections at Casarza.

The Cathodes, which consisted of thin copper sheets, 700 × 700 × 0·3 mm. [$27\frac{1}{2}$ × $27\frac{1}{2}$ × $\frac{1}{80}$ in.], were hung in the usual way from wooden rods by means of strips of copper, one of which was carried along the upper side of the rod direct to the main conductor, 30 mm. [$1\frac{1}{4}$ in.] thick, with which it made contact in the way described above (Figs. 112, 113).

The arrangements of the electrodes in the baths is shown in the scheme sketched in Fig. 114.

The baths themselves were lead-lined wooden vats, 2000 × 900 × 1000 mm. deep [6 ft. 6 in. × 3 ft. × 3 ft. 3 in.], of which

twelve were united in a group to be served by one dynamo. The method of joining together the wooden sides and the leaden

Fig. 115.
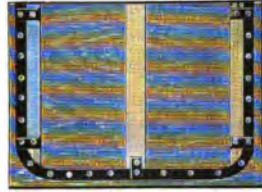
Fig. 116.

Method of attaching the lead linings to the vats (Casarza).
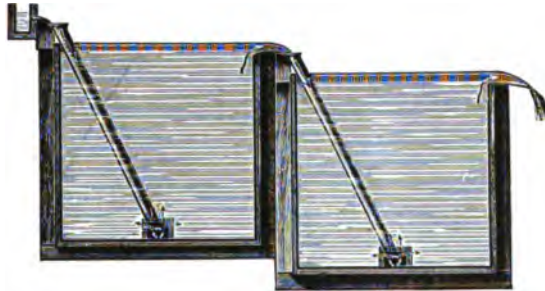
Fig. 117.—Section of vats, showing method of circulating the electrolyte (Casarza).
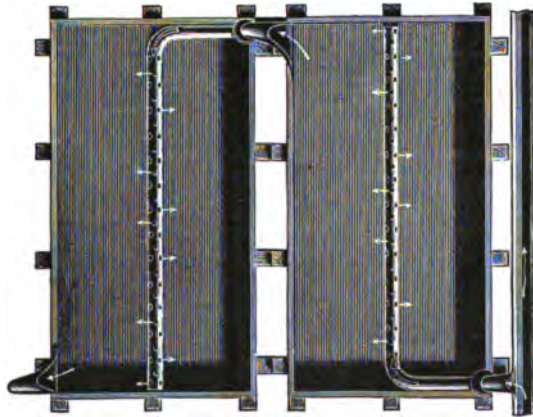
Fig. 118.—Plan of vats, showing method of circulating the electrolyte (Casarza).

linings of the vats at one and the same time is worthy of note. The lead sheet was screwed down with the wood instead of being

soldered therewith in the customary fashion.   Figs. 115 and 116
sufficiently explain this method of construction.

The **Electrolyte** consisted of an acid solution of copper and
iron sulphates, and was obtained by roasting a portion of the ore
and extracting the roasted material by water acidulated with
sulphuric acid.   The uniform circulation through the baths,
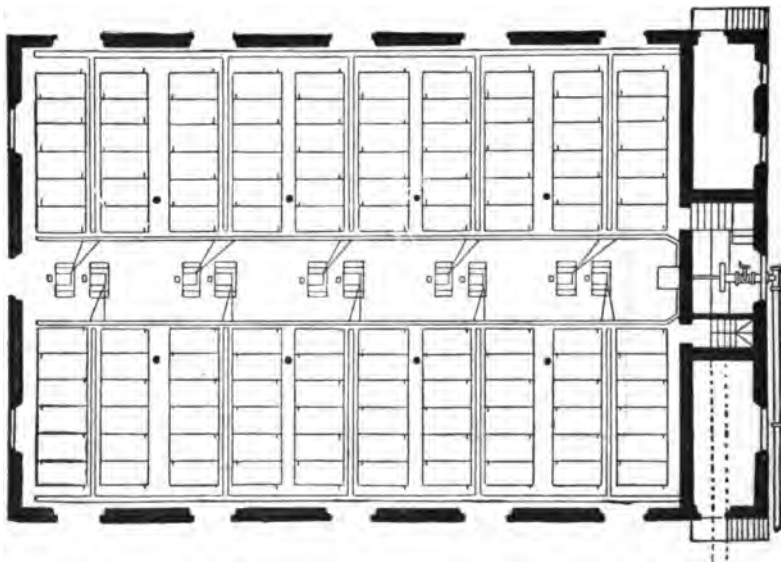
Fig. 119.—Plan of the Casarza installation.
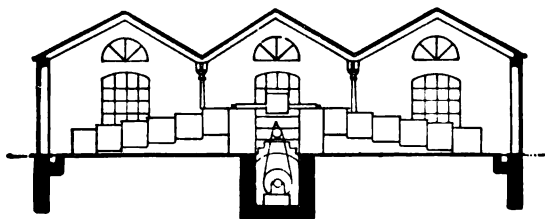
Fig. 120.—Cross section of the Casarza depositing-room.

which were arranged in step form, was brought about with the
aid of leaden pipes and of wooden channels on the bottoms of
the vats.   The solution flowed through a gutter to the vat which
stood at the highest level (Fig. 117), and, passing through the
whole length of this vat, overflowed into the next, as shown in
Figs. 117 and 118.   The arrangement of the installation is
illustrated in the accompanying three drawings, of which Fig.

119 is the ground plan, Fig. 120 the cross section, and Fig. 121 a general view of the interior of one of the depositing-room.

With anodes of such complex character, it is obvious that the *reactions which take place during electrolysis* must be of a very varied character. A decomposition of the sulphides of which the anodes are composed must precede the migration of copper, iron, or other material capable of forming ions. And this was

Fig. 121.—Interior of the Casarza depositing-room.

supposed to have happened partly through direct oxidation, and partly through the action of ferric salts, thus, *e.g.*:—

$$Cu_2S \; + \; 2Fe_2(SO_4)_3 \; = \; 2CuSO_4 \; + \; 4FeSO_4 \; + \; S.$$

Remembering the reactions, which Kiliani has shown to take place in the electrolysis of blister and refined copper, due to the impurities that gradually accumulate in the electrolyte, and that are here present in far greater quantity from the outset, it cannot require long consideration to decide that a considerable proportion of electrical energy must be wasted through changes, which take place both in the solution and upon the anode itself.

It is unnecessary here to enter upon a calculation of the **electromotive force** that should be required for this process. It will suffice to point out that after preliminary experiments, 1 volt per bath had been fixed upon as the *maximum* that could

be necessary, and on this assumption Marchese based his whole estimate of the cost of the undertaking. But as the account (to be given shortly) of the experience gained by the *Aktien-gesellschaft für Bergbau, Blei- und Zinkhüttenbetrieb* at Stolberg
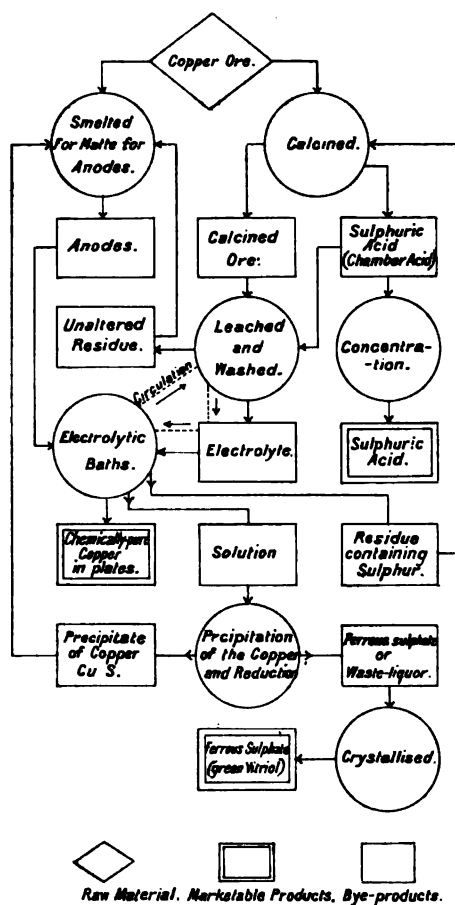
Fig. 122.—General scheme of the Marchese process.

(Rheinland) will show, the expenditure of power increased very considerably even after a short time of action.

In 1885, Marchese published an account of a nine-day trial that was made in that year with the experimental-plant, but he makes no mention of this fact, ascribing the increased expenditure of energy to some bad contacts that had been overlooked (!) by

the operator. At that time Marchese still estimated a net profit of 75 per cent. upon capital outlay on plant in a factory of this character. The scheme for the systematic treatment of ores by the Marchese system is shown in Fig. 122.

In addition to the above-mentioned *faults* of this system, the great fragility of the matte anode-plates is a serious difficulty. Then there occurred a separation of insoluble and non-conducting material on the surface of the sulphide, and small cavities gradually developed into deep pits during the progress of the electrolysis. And both these circumstances caused irregular solution of the anode, increase in the resistance, premature crumbling of the plates, inferior extraction of the anode-material through the formation of a crust of insoluble matter, and other actions prejudicial to the working of the process. In place of the electromotive force which had been calculated as sufficient for the satisfactory operation of the plant, it frequently became necessary to employ double, or even three or four times that voltage, in order to avoid the absolute stoppage of the work.

These last remarks have been reproduced from a paper written by the author in 1893 [*] on the direct electrolytic treatment of ores and metallurgical products. At the same time he gave an account of his own experiments with ore and matte in the years 1883 to 1887. He added that these negative results were obtained after a series of experiments, lasting over a few weeks, and conducted with the aid of a 1 H.P. engine, and yet they established everything that the 125 H.P. plant at Casarza had shown.

The Stolberg Installation.—The Stolberg Company also determined relatively quickly upon experiments with a large plant. Laboratory experiments having given promising results, a plant was first run for several months with a 5 volt × 150 ampere dynamo, or, in other words, with a current sufficient to determine either the conditions for, or the impracticability of, working on a large scale. This plant was inspected by Marchese; and then, after some deliberation, the erection of a plant of sufficient capacity to deposit 10 to 20 cwts. of copper in 24 hours was determined upon. It consisted of 56 baths, such as have been already described, consisting of lead-lined wooden vats 7 ft. 2 in. long, by 3 ft. 3 in. wide, by 3 ft. 3 in. deep.[†] Each bath contained 15 anodes and 16 cathodes, arranged in parallel, and at a distance of 2 in. apart.

The anodes at Stolberg were prepared from mattes of three different grades of concentration, containing respectively 7 to 8 per cent., 15 to 20 per cent., and about 50 per cent. of copper.

[*] *Berg- und Hüttenmännische Zeitung*, 1893, vol. lii., pp. 251, 269.
[†] This and the following account of the results of the Stolberg experiments are taken from an account published, with the sanction of the *Stolberger Gesellschaft*, in the *Zeitschrift für Elektrochemie*, 1894, p. 50.

Of these, the second was used directly for the production of the anodes, the first was concentrated by roasting and fusing with silicious materials, and the third was employed for the preparation of the solutions. The composition of two separate samples of the matte, as used for the anodes, is given in the following table, and as the composition was variable, a third column is appended, showing the average of a large number of analyses made at a later period than the others:—

TABLE SHOWING COMPOSITION OF ANODES USED AT STOLBERG.

	Analysis at Stolberg.	Analysis at Genoa.	Average Composition.
	Per cent.	Per cent.	Per cent.
Copper (Cu), . . .	17·20	24·78	15 to 16
Lead (Pb), . . .	23·70	12·74	14
Iron (Fe), ...	29·18	34·23	41 to 42
Sulphur (S), . . .	21·03	27·94	25
Sulphuric anhydride (SO_3),	0·69	...	...
Silica (SiO_2), . . .	0·88	...	...
Silver (Ag), . . .	0·0623	0·056	0·05

The anodes were 80 cm. high by 80 cm. wide by 4 mm. thick [2 ft. 7½ in. × 2 ft. 7½ in. × ¼ in.]. They were made by allowing the melted matte to flow out of the furnace into a large iron tank, from which it was removed by iron ladles and cast in iron moulds. The moulds were sunk in the ground so that the sulphides might cool very slowly, as otherwise the anode plates developed cracks, and were easily fractured. A long copper strip 2 cm. wide by 3 mm. thick [¾ in. × ⅛ in.] was laid in the mould before pouring, so that it might be cast into the anode, into which it penetrated to about the centre. The free end of the strip, outside the bath, was bent over and fastened by a screw clamp to the positive conductor, which consisted of a copper rod of about 3 cm. [1·2 in.] diameter, and so served to make electrical connections with the matte. To avoid rupture of the anodes under their own weight, for each weighed about 2¼ cwts., they were supported upon two strips of wood placed beneath them in the bath.

The cathodes consisted of copper plates 80 cm. by 80 cm. by 1 mm. [2 ft. 7½ in. × 2 ft. 7½ in. × 0·04 in.], with four strips of copper 2 cm. [0·8 in.] wide riveted to each, in order that they might be attached to cross strips which were laid upon transverse wooden slats placed above the vat. The connections of copper strips with the negative conductor were like those adopted for the anodes.

The electrolyte was made by extracting the richest mattes

(those carrying about 50 per cent. of copper) with dilute sulphuric acid, and when ready for use contained about 27 to 28 grms. of copper and 15 grms. of iron per litre [about 4½ oz. of copper and about 2½ oz. of iron per gallon]. In order to facilitate the constant circulation of the solution during the course of electrolysis, the vats were arranged one above the other in terrace form, and a pipe of 2 in. internal diameter led from the bottom of one vessel to the rim of that next below.

Two Siemens and Halske dynamos of the CF_{17}-type, of a size sufficient to deposit 5 cwts. of copper in 24 hours, were used to produce the necessary current. These dynamos, running at 700 and 800 revolutions, gave a current of 430 amperes × 35 volts. The current density in each bath was about 30 amperes per sq. metre [2·8 amperes per sq. ft.], and the electromotive force required was at first 1 volt per bath.

The profits to be earned by the process were estimated by Marchese in the following way:—Starting with a matte containing 15 to 20 per cent. of copper, 14 per cent. of lead, and 0·05 per cent. of silver, and expecting to recover all these metals (the copper by direct electrolysis, and the other two from the insoluble anode residue by a subsequent treatment) he arrived at the following results. In the ton of matte he reckoned :—

150 kg. of copper at Fr.	1·3	=	Fr.	195
140 kg. of lead at Fr.	0·25	=	Fr.	35
0·5 kg. of silver at Fr.	180	=	Fr.	90
Value of 1 ton of matte		=	Fr.	320

But he was able to purchase the matte at Fr. 112·5 per ton, because only the copper contents were taken into account, and he thus reckoned upon obtaining at once a clear gain of Fr. 207·5 per ton of matte, or Fr. 1383·33 per ton of copper. The interest upon the capital locked up in the shape of copper in the baths was thus estimated : there were 20 anodes of 125 kg. each in every bath, and as there were 58 baths, the total weight of anode material was 145 tons ; and this represented (in round numbers, at Fr. 100 per ton) Fr. 14,500. But the anodes gradually gave up their copper during the electrolysis, and he therefore took the half of this sum as the average value of the material in the baths throughout the operation, and so arrived at the sum of Fr. 8000.

Then 580 kg. of copper were deposited daily in the 58 baths. But since three months were required to produce copper plates of the usual marketable thickness, there remained in the baths $\frac{90}{2} \times 580 = 26,100$ kg. of copper (because here also the half of the total copper is taken as an average); and the value of this is Fr. 32,000. The percentage of the copper in the solution itself was so small that it was regarded as negligible. The result of this calculation is that an annual production of 210

tons necessitates the sinking of a capital of Fr. 40,000 in the form of copper in the baths. But since the electrolytic copper recovered is chemically pure, it is estimated as being worth Fr. 125 to 140 more per ton than is the ordinary copper of commerce. And this, calculated on the annual outturn of 210 tons, amounts to nearly Fr. 30,000, which is equivalent to an interest of 75 per cent. on the capital of Fr. 40,000.

The Stolberg plant when at first set in operation, fulfilled all expectations; the baths worked satisfactorily, and the separated copper was pure. After a few days, however, the resistance of the baths began to increase, and required, in some instances, an electromotive force of 5 volts. The primary cause of this increase was a dense deposit of separated sulphur at the anode, which hindered the access of the electrolyte to the undecomposed sulphide within. But there was a still greater difficulty to be encountered. The copper and iron being dissolved out of the anodes, they lost all cohesion, so that large fragments crumbled away and filled up the space between the anodes and cathodes at the bottom of the vat. There they formed a short-circuit for the current, because their conductivity was higher than that of the electrolyte, and the bath remained undecomposed. Finally, polarisation must have added considerably to the apparent resistance of the bath. The fact that such polarisation existed is proved by the observation that a lower E.M.F. was required for the operation of baths that had been cut out of the circuit for a few days. A modification of the process suggested by the last-mentioned observation was tried, but was soon given up again. Then, as the formation of PbO_2 was considered to be the cause of the polarisation, the percentage of copper in the anodes was increased, and that of lead diminished, but with no better result; a change in the proportion of iron also failed to produce any improvement. Further, the deposited copper was found to contain antimony, bismuth, lead, iron, zinc, and sulphur. Hence it was determined to abandon the use of matte for anodes, in favour of lead, which would be insoluble. A small-scale experiment was therefore tried, and as the results were satisfactory, a larger bath was erected. The electrolyte employed was the same as had been used in the Marchese baths, only it had the advantage of remaining serviceable for a longer time, because the proportion of iron that it contained was not being constantly increased through the action of the solution upon the anodes. The E.M.F. required was 1·7 volts; and the results were at first good. But in a short time the quantity of copper deposited fell to 60 per cent. of that which should theoretically have been obtained, and the potential rose to 2·15 volts.

Use of Depolarisers.—The cause of this defect also lay in the polarisation of the anodes, which became coated with PbO_2

under the oxidising influence of the current, and so yielded a back-electromotive force that opposed and weakened the electrolysing current. It was then hoped that the introduction of a reducing agent would eliminate this source of trouble. Sulphurous acid was selected for the purpose, and was led into contact with the anodes that it might combine with the oxygen separated there, and so form sulphuric acid. A small experiment was therefore made with a bath containing four lead anodes of 0·37 sq. metre [4 sq. ft.] surface area and four copper-coated lead cathodes of like dimensions. The electrolyte contained per litre 39 grms. of copper, 14·4 grms. of iron in the ferrous state, 3·9 grms. of iron in the form of ferric salts, and 9·6 grms. of free sulphuric acid.* The sulphurous acid was obtained by burning sulphur, and, mixed with air, was injected into the bath. The E.M.F. required was not diminished through the introduction of the reducing agent, but the yield of copper was increased, and the metal was purer, containing 99·984 per cent. of copper. A large quantity of sulphuric acid was, of course, formed, and this extracted so much soluble material from the copper mattes that trouble was caused by the crystallisation of salts in the baths. It should here be added that a patent † was granted for the use of sulphurous acid as a depolarising agent in 1885. A larger bath was then arranged on the lines of the experimental apparatus. At first the gases from matte-calcining furnaces were led into the baths to provide the sulphurous acid required; but the gases were found to be too dilute, and were, therefore, replaced by those from the muffles used in the calcining of zinc ores. But various circumstances (among others, the offer of a new process by Siemens & Halske) interfered with the prosecution of the work in this direction, which would have involved the transfer of the whole plant. The use of insoluble anodes, and of the depolarising agent, was a great departure from the original Marchese process, and it is· to be regretted that the experiments which were set on foot could not be carried through; experiments, however, with other depolarisers, both at Stolberg and in other installations, have not as yet led to satisfactory results.

Body's Process.—In working the Marchese process, it was remarked that a part of the current was used up in converting the ferrous sulphate present in the liquors into the corresponding ferric compound, and that this salt again attacked the anode material. It was, therefore, only natural that more attention should be given to the action produced by iron salts, with the object of utilising it in some convenient way. The first step in this direction, at least, in connection with electrolytic processes,

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* [This is equivalent to about 6½ ozs. of copper, 2¾ ozs. of ferrous iron, ½ oz. of ferric iron, and 1½ oz. of sulphuric acid per gallon of liquid.]

† German Patent 32,866, March 13, 1885.

is to be found in a patent granted to Body*; but in purely metallurgical works the utilisation of iron salts had, of course, long been known. Although Body's apparatus and process are not concerned with copper extraction alone, but were intended for the electrolytic extraction of metals from ores in general, they may be here described as being the forerunner of the well-known processes of Siemens & Halske and Hoepfner.

The vessel, A (Figs. 123 and 124), is made of Portland cement, and is painted within and without with an impermeable material. The partition walls, S, which are also of Portland cement, do not reach quite to the bottom of the bath; and in the space thus left beneath them are placed plates of some material (like felt) that is pervious to water. The raised floor is covered with a carbon plate, C, in connection with the positive pole of an electrical generator; and the inner surfaces of the
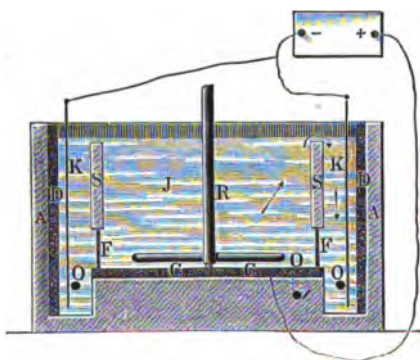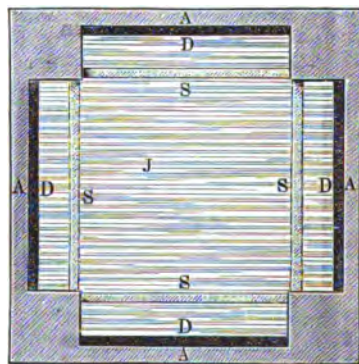
Fig. 123.   Fig. 124.

Body's apparatus.

outer walls of the vessel are also lined with carbon, D, which, however, is practically unnecessary. The metal plates, K, which form the cathodes, are suspended in the space outside the partitions, S. A solution of ferric salts with sodium chloride is used as electrolyte. The ore, which has been previously moistened with a similar solution, and is still saturated with it, is placed in the inner space, J, and is here kept in constant motion during electrolysis by means of the stirrer, R. The solution enters through the opening, O, in the raised floor, follows the course of the arrow marked in the figure over the partitions, S, and, finally, after traversing the cathode compartment, escapes through the aperture, O, in these outer chambers.

While the solution is thus slowly circulating the following reactions take place :—

* U.S.A. Patent 33,815, Jan. 5, 1886.

1. The metals contained in the ore are brought into solution at the expense of the ferric salts in the electrolyte, which are thus reduced to the ferrous state.

2. The dissolved metal is deposited at the cathode.

3. The chlorine which is set free at the anode peroxidises the ferrous salts that have been produced, and any excess of chlorine that may escape absorption in this way is able to act directly upon the ore.

The Siemens-Halske Matte-Refining Process.—Siemens & Halske then went a step beyond this, and caused the reactions between the ferric salts and the copper compounds to take place entirely outside the electrolytic vessel. *They stored up, so to speak, the anode energy in a part of the electrolyte* in order that they might utilise it outside the baths. The process was thus described in the first German patent taken out by the firm.*

The powdered copper pyrites is roasted at a moderate temperature, preferably in a Gerstenhöfer furnace, in such a way that the iron is almost completely oxidised, whilst the copper is contained in the roasted material, partly as copper sulphate, and partly as copper oxide, but mainly as cuprous sulphide. The finely-divided material, after calcination, is treated with the solution flowing from the electrolysing tanks. This leaching is best performed in a series of vats, through which the liquid flows successively in such a manner that it passes last through the vat that was latest charged with the ore. The solution, which is thus newly enriched with copper sulphate, and no longer contains any ferric salt, is now returned to the electrolytic cells, where it is first deprived of its copper, and is then peroxidised, so that it may be used afresh to extract the copper from another charge of ore. The process is therefore continuous, and the same solution may be used repeatedly until, owing to the absorption of foreign metals previously contained in the ore, it has become too impure for the process of electro-deposition.

This solution, for use in separate electrolyte cells, should be introduced continuously nearly at the bottom of the cells which surround the cathode plates; then rising to the top of these, and depositing a part of its copper by electrolytic action on the cathode on its way, it flows over the top rim of the membrane into the anode compartment, through which it passes to make its final escape from the bottom of this cell (Fig. 125). During the passage of the electrolyte through the anode cell, the ferrous sulphate that it contains is first converted into a basic ferric sulphate, which in turn is changed into the normal ferric sulphate by the absorption of sulphuric acid produced through

* German Patent 42,243, Sept. 14, 1886. [English Patent 14,033, Nov. 1, 1886.]

the electrolysis of the copper sulphate; the higher specific gravity of the latter salt causes it to sink to the bottom of the vessel. The liquid escaping from this compartment, therefore, contains less copper than was present in it when introduced into the cathode cell; and it also contains neutral ferric sulphate in solution. This solution has now the power of converting cupric and cuprous sulphides and copper oxide into copper sulphate. In thus acting upon the first-named copper compound the ferric sulphate is reconverted into ferrous sulphate, whilst the liberated oxygen serves to oxidise the sulphide of copper. The product from the roasting of the ore at a low temperature, as above explained, contains most of its copper in the form of sub-sulphide; but the iron is present as peroxide, a substance which is not attacked by ferric sulphate, and is scarcely affected by sulphuric acid. The cuprous sulphide, however, is energetically dissolved by the ferric solution.

Fig. 125. — Siemens & Halske electrolytic cell for treating copper ore.

The chemical processes, which take place during the electrolysis, and the leaching process are clearly shown in the following equations :—

I. $\quad x H_2 SO_4 + 2 CuSO_4 + 4 FeSO_4 = 2 Cu + 2 Fe_2(SO_4)_3 + x H_2 SO_4$

II. (a) $x H_2 SO_4 + Cu_2 S + 2 Fe_2(SO_4)_3 = 2 CuSO_4 + 4 FeSO_4 + S + x H_2 SO_4$

(b) $\quad\quad\quad\quad CuO + H_2 SO_4 = CuSO_4 + H_2 O$

(c) $\quad\quad\quad 3 CuO + Fe_2(SO_4)_3 = 3 CuSO_4 + Fe_2 O_3$

(d) $\quad\quad CuO + 2 FeSO_4 + H_2 O = CuSO_4 + (Fe_2 O_3 + SO_3) + H_2$

A comparison of the equations I. and II. (a), shows that if the ore hold all its copper in the form of cuprous sulphide, the electrolyte, after passing through the leaching vats, will contain exactly the same quantity of copper sulphate, ferrous sulphate, and free sulphuric acid as it did prior to electrolysis; and that it is, therefore, completely regenerated, and may be used again for the electrolytic decomposition. But if the copper be present in the ore partly as copper oxide, it is evident from equations II. (b), (c), and (d) that in this case the solution will be richer in copper, but poorer in respect of iron and sulphuric acid than it was before electrolysis.

It is not necessary to point out that the raw matte may be used in lieu of the roasted material, because the copper is present almost entirely in the form of cuprous sulphide. In this case, however, iron would also be dissolved, and a complete

uniformity of the solutions in regard to copper and iron could not be maintained. It is to be remarked that in the described electrolytic process no polarisation occurs, and that the position of the two electrode materials in the electro-chemical series gives rise to no counter electromotive force.

Whilst, with matte anodes, an E.M.F. of 1·5 volts is necessary to give the required current density, 0·7 volt will suffice when the above process is adopted. And, again, whilst in the former case, about one-third of the current volume is used for other reduction processes, and is therefore lost; by the alternative method there is no loss whatever of this nature.

In order to produce the rapid circulation of liquid through the vats, which is necessary for satisfactory work, the cells are placed in terrace form (Fig. 126), and all the cathode compartments, K_1, K_2, K_3, are connected together by siphons, h_1, h_2, h_3, in one
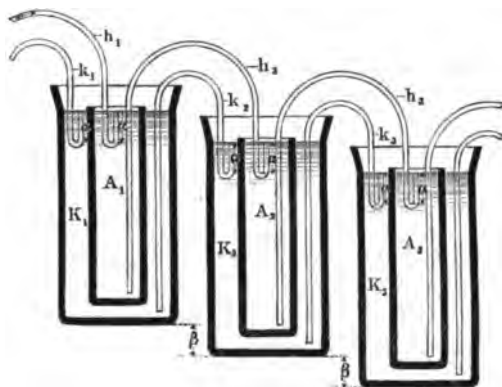
Fig. 126.—Arrangement of vats in the Siemens-Halske process.

group, while the anode cells, A_1, A_2, A_3, are similarly connected in another series by the siphons, k_1, k_2, k_3. In order to maintain the level of liquid in the vessels independent of the quantity of solution added, the ends of the siphons in the lower vats are turned upwards for the space, a, which is equal to the difference in height, β, between two consecutive vessels.

Modified Siemens-Halske Process.—From a subsidiary patent * taken out by the same firm, it must be concluded that the use of this process led to difficulties. The electrolytic cells had previously been divided into two (positive and negative) compartments by a membrane; but it is shown in the second patent specification that these membranes are liable to become torn during electrolysis. The membranes have either too high

* German Patent 48,959, Jan. 3, 1889. [English Patent 3533 Feb. 27, 1889.]

an electrical resistance, or else they are not sufficiently durable, for they stretch and allow the solutions to escape.

Figs. 127, 128, and 129 show an electrolyte cell in which this

Fig. 127.
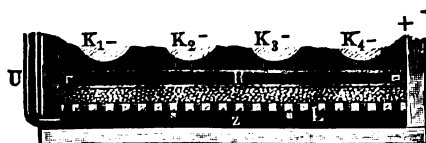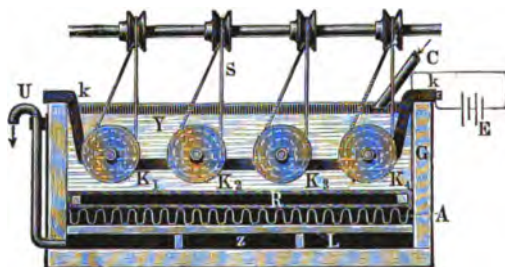
Fig. 128.
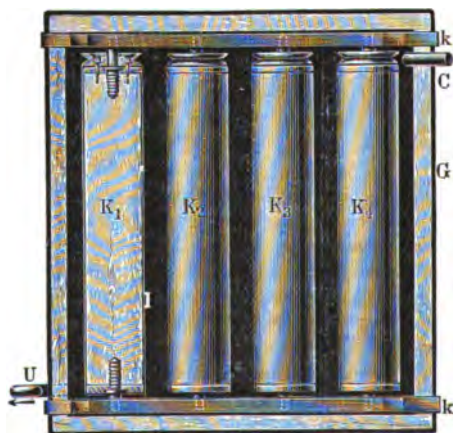
Fig. 129.

Siemens & Halske's electrolyte cell (1889).

evil is remedied. A flat vessel, G, made of wood or of other suitable material, and coated with lead, is provided with a perforated false bottom, L, on which the anode, A, is extended. The anode may consist, either of plates of retort carbon in direct

electrical connection with one another, or of perforated lead plates covered with small fragments of retort carbon, or, finally, of deeply corrugated lead plates containing perforations to allow of the passage of the electrolyte. The horizontal anode is provided with the necessary insulated electrical connections, and is covered with a layer of some filtering material that may serve to prevent the escape of the solution surrounding the anodes The filter may be of felt or any other suitable organic or inorganic material. The cathodes consist of the surfaces of the cylinders, K, which are quite covered by the electrolyte, and are constantly maintained in slow revolution by the waterproof belt, S. These cylinders may be made of a wooden core coated with wax, cement, or other material, and surrounded with a conducting material, which is electrically connected in any suitable way with the journals of the cylinders and the conductors, k.

The regenerated solution, consisting of copper and ferrous sulphate solutions, is conveyed in a continuous stream into the liquid which is already covering the cylinders. The rotation of the latter effects the continual mixture of the solution down to the partition separating it from the anode compartment. The tube, U, conducts the solution away from the space beneath the filter at the same rate as the regenerated liquor is run into the upper compartment through C; and, there is, in consequence of this, a constant but slow transference of liquid through the filter from the cathode to the anode compartment. Here the ferrous salt is reconverted into ferric sulphate by the liberated oxygen, and the ferric salt, having a higher specific gravity, sinks to the bottom and is at once carried away through U, so that by properly regulating the inflow of liquid, the strength of the current, and the quantity of copper and iron in the solution, the result of the process should be that the electrolyte in the upper compartment loses some two-thirds of the copper contained in it, while in the anode portion the whole of the ferrous salt is peroxidised to the ferric state. The solution is uninterruptedly conveyed from the anode cell to the extraction tank, and after acting upon the ore powder, it circulates through the whole system again.

According to later accounts * the anodes were afterwards made of specially prepared homogeneous round carbon rods, a (see Figs. 130 and 131), of which every 109 were bound together into one group by means of a thoroughly insulated cast-lead frame, forming a system 1600 mm. long by 405 mm. wide [5 ft. 6 in. × 1 ft. 4 in.]. The connection with the main conductors is made by means of the lead strips, V, cast on to the frames.

The electrolyte vessels are shallow wooden tanks rendered

* Grusonwerk-Magdeburg. *Das Siemens'che Kupfergewinnungsverfahren aus Erzen.*

watertight by a lining of asphalted jute. The anode system is placed upon the floor of the tank, and the waste pipe is fso placed that it may readily conduct the solution away from the apparatus. At a certain distance above the anode is the linen filter, F, stretched upon wooden frames, and serving to separate the bath into two compartments, one above the other. In the upper or cathode compartment are placed the wooden plates, K, which cover the whole area of the vat, and are overlaid on the underside with thin sheet-copper to receive the electro-deposited metal. Between these cathode plates and the filter the cathode solution is kept thoroughly mixed by means of a mechanical
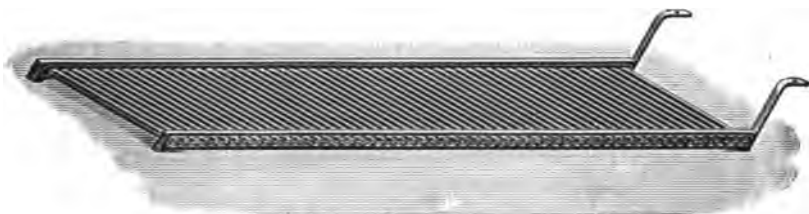
Fig. 130.—New form of anode (Siemens-Halske).
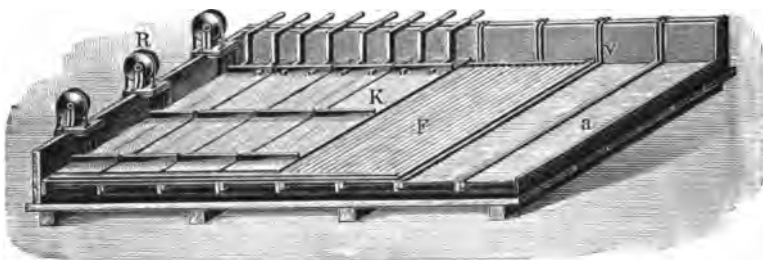
Fig. 131.—Newer form of tank (Siemens-Halske).

circulating arrangement, actuated by the pulleys, R, on the edge of the vessel.

These processes were put to a practical test in Stolberg by the above-named company, but it is evident from Cohen's account that only a very imperfect apparatus was employed. The want of durability both of the membrane separating the anode and cathode compartments, and of the carbon anode rods, difficulties in the clearing of the turbid solution obtained on extracting the ore with the anode liquors, and all the derangements that resulted from these troubles, caused an unforeseen increase in the E.M.F. required (from 0·75 to 1·8 volts per bath), and finally led to the suspension of the experiments. From a private communication from Messrs. Siemens & Halske, the author learns that

the difficulties encountered in the Stolberg experiments have been entirely overcome in a new installation of the apparatus, owing to the experience gained in the operation of a large experimental plant at Martinikenfeld, near Berlin, in a trial of several years' duration. An installation on this system is at present in course of erection at Peña de Hierro in Spain.

The Hoepfner Process.—Another theoretically very interesting process, based on the same princ ple as that of Siemens, has been worked out by Hoepfner,* who recorded the results that he had then obtained in a paper read before the Upper Silesian Society of Applied Chemistry,† from which the following account is taken :—

"I use electrolytic tanks, which are separated by reliable diaphragms into anode and cathode compartments, and which permit a through circulation from anode to anode, and from cathode to cathode, through any number of cells placed in series. In the anode compartments are carbon anodes, which are incapable of electrolytic solution, and in the others are cathodes of sheet copper. A solution of cuprous chloride in brine or in calcium chloride solution, or the like, flows past a number of anodes in turn; and a similar solution comes into contact successively with any convenient number of cathodes. Metallic copper is deposited upon the latter at the rate of 2·36 grm. [36·42 grains] per ampere per hour, that is at exactly double the rate at which the same current can deposit the metal from the solution of a cupric salt, such as copper sulphate.

"At the anode, if no cuprous chloride were present, free chlorine would be liberated; and an E.M.F. of 1·8 volts would then be necessary for electrolysis. But the chlorine in this process combines at once with the adjacent cuprous chloride, and converts it into cupric chloride. In this way an E.M.F., amounting to nearly 1 volt, is produced in a direction favourable to the action in the electrolyte; so that the electrolysis is practically accomplished with a difference of potential of only 0·8 volt between the electrodes. The solution in the cathode cells becomes weaker and weaker in respect of copper as it passes through them successively, until finally it flows from the last of the series nearly free from copper. Leaving the electrolytic vats, it is collected for the above described process of circulation through the ore. The anode solutions retain their copper, but no longer as cuprous chloride; for it has become converted into cupric chloride, and the solution containing the latter salt flows continuously from the vat.‡

"The cupric chloride solution thus coming from the anodes is

* German Patent 53,782, March 1, 1888. [English Patent, 4626, March 26, 1888.]

† *Zeitschrift für angewandte Chemie*, 1891, p. 160.

‡ *Ibid.*, 1890, p. 622.

used in the system of circulation to extract the copper and silver from the finely crushed ores of these metals. Large leaching vats of about 10 cb. m. [350 cub. ft.] capacity are used; they should be suitable for the treatment of the material with heated solutions, and should be provided with a good stirring apparatus. The solution acts upon copper ores according to the equation :—

$$CuCl_2 + CuS = S + Cu_2Cl_2$$
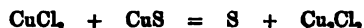
So that the cupric chloride, by combining with copper, becomes reduced to cuprous chloride. It is well known that silver sulphide, Ag_2S, is readily attacked by cupric, and even by cuprous, chloride, so that when this substance is present in the ore, it is converted into chloride, as shown in the following equation, and the silver chloride that is formed dissolves in the chloride liquor :—

$$Ag_2S + 2CuCl_2 = Cu_2Cl_2 + 2AgCl + S.$$

"The regenerated cuprous chloride solution is treated, as described below, for the separation of silver, arsenic, bismuth, and other substances, which would render the deposited copper impure, and is then caused to flow to the anodes and cathodes. At the former, cupric chloride is produced, whilst at the latter the separation of copper takes place.

"The purification of the solution is most readily and practically effected by chemical means, cupric oxide or lime being employed to remove the arsenic, antimony, or bismuth, which are known to be especially prejudicial to copper, so that the metal ultimately deposited may be pure. The silver is separated, either electrolytically or chemically before the copper. Any small proportion of iron that may have become dissolved from the copper ores is separated by the treatment with lime; if this separation were not effected, the proportion of iron would gradually increase, and hence the solubility of the cuprous chloride would be reduced to about one-quarter of its former value. Cuprous oxide is such a powerful base, that even the oxide of zinc is precipitated before that of copper on the addition of alkali or alkaline earths to solutions of cuprous chloride.

"The quantity of copper deposited in 24 hours in a sufficient number of baths, with an interpolar E.M.F. of 0·8 volt, is equivalent to 43·9 kg. [96·6 lbs.] per H.P. (= 690 ampere hours), allowing for a loss of 10 per cent. Since each horse-power developed in large works only requires an expenditure of 22 kg. [48·5 lbs.] of coal *per diem* in the boilers, it may be estimated that in a well-managed installation, each pound of coal burnt should produce 2 lbs. of deposited copper. Allowing for the crushing of the ore and the work of stirring, 1 lb. of coal should suffice to produce 1 lb. of copper from the original ore. The extraction of copper ought, therefore, to be possible even in

countries in which the coal resources are of the most limited character.

"The above-described process, which is shortly to be applied in many places both in Germany and abroad will, as I [Hoepfner] hope, quite displace the ordinary process of copper-smelting.

"According to my [Hoepfner's] calculation, a daily production of 1000 kg. [1 ton] of copper from a 5 per cent. pyrites would require a capital outlay of about 123,000 marks [£6150], and the daily working cost of such an installation, inclusive of interest and amortisation charges, would be about 190 marks [£9, 10s.]. The daily working cost of all other processes hitherto used would, under otherwise similar conditions, be more than double this amount.

"The causes contributing to the cheapness of the present process may be stated as follows :—

"1. The greater depositing power of the current in the cuprous solution, affording twice as much copper per hour as would be possible with a sulphate process ; so that the cost of the electric installation is reduced by one half.

"2. The higher efficiency of the chloride solution, which is able to extract from the ore all the valuable metals that it contains.

"3. The considerable dissolving power of this solution (which may take up as much as 150 grms. of copper per litre [1½ lbs. per gallon]), in consequence of which the leaching plant may be of comparatively small size and demands the expenditure of but little mechanical power.

"Although I [Hoepfner] venture to consider the described process as already [1891] proved to be sound, there is a possibility that it may be even yet improved, so that the cost of production may be still further reduced."

Unfortunately, the hopes which Hoepfner at that time expressed have not been fulfilled, although the process was put to a practical test, both at the Schwarzenberg works in the Erzgebirge district of Saxony; and in two other installations at Giessen and at Weidenau (Siegen). The difficulties which militated against the success of the process* may be stated under four heads :—

1. For the complete extraction of the copper it is necessary that the ore, whether raw or roasted, should be crushed exceedingly fine. The cost of this crushing is, in some cases, far greater than would be compatible with the working costs permissible.

2. Since heat must be applied during the leaching process, it is unavoidable that a part of the dissolving power of the cupric chloride, generated during electrolysis, should be used up in extracting iron compounds from the ore whereby, at the same time, the electrolyte is quickly rendered impure.

3. The filtering and washing of the muddy residue is a very difficult problem, which has not yet been satisfactorily solved.

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* Compare Jensch, "Zur Elektrolytischen Gewinnung von Kupfer nach dem Hoepfner'schen Verfahren" in the *Chemiker Zeitung*, 1884, p. 1906. [*Journ. Soc. Chem. Ind.*, 1895, vol. xiv., p. 279.]

4. Durable, and at the same time inexpensive, materials for the diaphragms and the anodes do not appear to be as yet forthcoming, in spite of numerous patents that have been taken out in this connection.

These difficulties, certainly, cannot be considered insurmountable, and it is therefore to be regretted that the experiments at the Schwarzenberg works should have been stopped on account of the death of the owner.

[The Schwarzenberg Experiments.—The original account given by Jensch of his experience with Hoepfner's process at Schwarzenberg may not be available to many readers; and as it sets forth very clearly the details of the work a short abstract may be given here. The ore used contained from 9·5 to 12·25 per cent. of copper, and from 34·5 to 32·6 of iron; it was crushed so finely that on an average 85 per cent. of any sample would pass through a sieve with 200 holes to the linear inch, and 96 per cent. would pass a 100 sieve. The ore was leached in large revolving wooden drums, holding from 200 to 1500 gallons each, into which steam was admitted to hasten the reaction between the ore and the solution, the latter consisting of the cupric chloride from the anodes and calcium chloride. The drums gave considerable trouble owing to leakage, which increased with the rise of temperature and with the growing percentage of cuprous chloride in the solution. It was necessary to treat even the richer ores three or four times with the leaching solution; but with the poorer samples, although half of the copper was removed in the first extraction, ten or twelve were necessary to dissolve the remaining half. It was found also that a large excess of cupric chloride was necessary, because, at the temperature of the reaction, magnetic pyrites and iron pyrites are both attacked by this substance. The slimes were filter-pressed after the leaching in order to extract as much as possible of the solution from them. The anodes were of paraffined carbon, the cathodes of thin sheet copper, the use of copper-coated carbon cathodes having proved unsuccessful. The earlier difficulties with the parchment diaphragms were here met with. These diaphragms were previously described by Cohen as swelling up and becoming very tender after a few days' use, so that when the carbons disintegrated, as they did at the slightest provocation,* the fragments of the anode collected at the bottom of the bath and, pressing against the parchment, produced rupture.—TRANSLATOR.]

The Cohen Process.—The solution of the diaphragm problem appears to have been accomplished already, in course of

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* [It is claimed for the Street-Girard carbons (English Patent 13,339, 1893) that they are capable of resisting disintegration, so that they may be used in aqueous solutions, even with currents considerably exceeding 0·5 ampere per sq. in. in density. They are prepared by heating them electrically to a temperature at which they soften and are converted into graphite.— TRANSLATOR.]

some experiments made by Cohen,* who observed that when cuprous chloride was electrolysed under a low current-density, the cupric chloride formed at the anode sank to the bottom of the containing vessel in the form of a solution, of which the specific gravity was higher than that of the surrounding medium, and, collecting at the bottom, it formed a layer of gradually increasing thickness. If the cathode were so long that it dipped into this layer, copper became dissolved from the former within the immersed area; and the deposition of copper could be effected most satisfactorily without a diaphragm with the aid of the apparatus shown in Fig. 132. A carbon anode, A, is used of such length that it dips into a collecting-trough formed at the bottom of the bath, and it is suspended opposite a cathode of sheet copper, K, of only half its length. The cuprous chloride liquor is admitted into the upper part of the deep electrolysing

Cu₂ Cl₂ Solution.

Permanent Level of the Liquid.
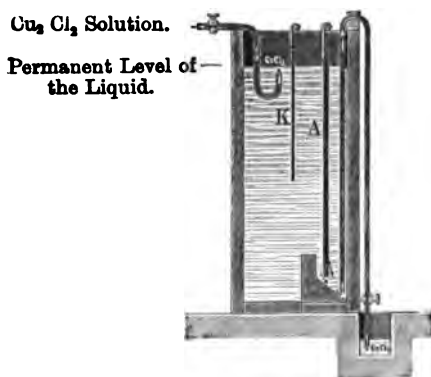
Fig. 132.—Cohen's single-compartment electrolyte cell.

vat, whilst the cupric chloride solution, which streams downward from the anode, is withdrawn through a siphon from the deepest part of the trough in which it collects. With a current density of 20 amperes per sq. metre of cathode area [1·86 amperes per sq. ft.] the deposit of copper answers all requirements in respect of both quality and quantity. The E.M.F. required under these conditions amounts scarcely to $\frac{1}{2}$ volt.

It is evident that the Hoepfner process, and possibly that of Siemens' also, has been advanced a stage by this very ingenious and simple device. But this is the last step towards the direct treatment of sulphide ores and metallurgical products of which any description need be given in this place. Of new suggestions and patents there is no lack; but they will remain for the most part as they are at present. And it may be said that the quest

* *Zeitschrift für Elektrochemie*, 1895, vol. ii., p. 25.

for a practical method for the direct electrolytic treatment of copper ores is still open.

Applications of Copper.—The uses of copper are very numerous on account of the valuable properties of the metal. Copper serves for the production of a large number of implements, apparatus, parts of machinery, and the like, both for household and for factory use; in electrical work it finds a special application in the form of wire. In the service of art it is used both in coppersmith work and in electrotyping. In the mixed-metal trades copper forms the basis of very many important alloys, such as bronze (including copper-tin, copper-tin zinc, copper - manganese, copper - aluminium, and copper silicon), brass (copper-zinc), German silver (copper-nickel zinc), &c. For the production of such copper compounds as, for example, copper sulphate, cupric oxide, phosphor copper, so far as they do not occur as bye-products in metallurgical works, metallic copper, and the scrap from the rolling mill and the coppersmith's works are commonly used.

CHAPTER II.

SILVER.

Properties of the Metal.—Silver (Ag; atomic weight = 108; specific gravity = 10·5) is a white, tough, malleable metal with a brilliant lustre, and a crystalline structure (in the regular system), and with a hardness intermediate between those of copper and gold. It has the highest electrical conductivity of all the metals. Its fusing point approximates 1000° C., and it is volatile at high temperatures, so that it may be distilled in the oxyhydrogen flame. A special characteristic of silver that is of great importance in connection with the refining and working of the metal is its power of dissolving oxygen when in the liquid state. At the moment of solidification, and after a thin crust of solid metal has formed over the surface, the oxygen which is given out from the still fluid metal within, forces its way through the outer crust, and often gives rise to a considerable loss of metal by the projection of small fragments to a distance; the phenomenon is known as the spitting, sprouting, or vegetation of silver. Among the metals which dissolve, or are dissolved by, silver, lead, mercury, copper, and zinc may be especially noted.

Silver belongs to those metals which cannot be oxidised directly either at high or at low temperature, either in moist or in dry air. Of the metalloids, the halogens, and especially chlorine, are most liable to combine with silver; but it may be

very readily united also with sulphur by direct fusion. Among the compounds of sulphur, hydrogen sulphide is able to attack this metal energetically. The best chemical solvents are nitric and concentrated sulphuric acids. Many metallic chlorides ($CuCl_2$, $HgCl_2$, $FeCl_3$) are capable of converting silver into its chloride, and so of making it soluble in other salts; cyanides also can form double salts, which are soluble in water by direct action upon either metallic silver, its haloid salts, or its sulphide.

Occurrence of Silver in Nature.—Silver is found native; alloyed with gold, copper, and mercury; as chloride in horn silver, $AgCl$, as bromide and iodide in bromargyrite ($AgBr$), and iodargyrite (AgI) respectively; as sulphide in silver glance, Ag_2S, and in combination with other sulphides, as in the case of red silver ores and fahlerz which may be given as examples of thioantimonites and thioarsenites. It is also present as sulphide in more or less considerable quantity in nearly all the sulphide ores of other metals. The extraction of silver is effected according to one (or to a combination) of the following principles :—

1. Solution of the silver in another metal, with subsequent concentration and separation.
2. Separation of the silver by processes of chemical solution, sometimes with subsequent chemical precipitation.
3. Electrolysis.

1. SOLUTION OF THE SILVER IN ANOTHER METAL.

Treatment with Lead.—Excepting in the case in which a material containing much zinc or copper has to be treated (such a material being subjected directly to the third process), the silver is obtained as an alloy with lead from most silver ores or metallurgical products, either by smelting with lead ores or by contact with a bath of metallic lead.

For smelting with lead ores, only a poor material is used, and in no case would the proportion of silver exceed 10 per cent. The smelting processes employed will be very briefly described in the Chapter on *Lead*. In order, as far as possible, to avoid loss of silver, an alloy (work-lead) with less than 1 per cent. of silver should be produced; this is then submitted to a process which results in the silver being concentrated in a small portion of the lead, whilst the remainder of the latter is worked up into a soft or market lead, which should be almost free from silver.

The concentration process may consist in melting the work-lead and submitting it to a series of systematic crystallisations, the lead crystals being ladled out from the bath as fast as they form, or else the still fluid alloy of lead and silver (which now contains a larger proportion of the latter metal) is tapped off from the purer lead crystals at a later stage, and nearer to the

time when the whole mass would solidify.   By this method,
which is known as the Pattinson process, an alloy containing
somewhat less than 2 per cent. of silver is formed, and this is
afterwards treated for the separation of the two metals.   Another
concentration process [the Parkes process] is based on the solu-
bility of silver in zinc when the fused lead alloy is mixed with
a small proportion of melted zinc, and the separation of a ternary
alloy of silver, zinc, and lead, which is less fusible than lead
itself.   The crust of zinc alloy which forms on the surface of the
lead on cooling the mixture a little, is removed and heated by
itself so that the excess of lead may liquate out, and the residue
is then distilled, or it is treated, when in the molten condition,
with a current of water vapour.   In the latter case zinc oxide is
obtained mixed with grains of a rich silver-lead, and is separated
from the remaining melted silver-lead alloy, washed, dried, and
sold for use as a pigment.   The residue from the washing
operation is purified with sulphuric acid, and is submitted with
the bulk of the silver-lead to the separation process.   This
process is distinguished from that of Pattinson by a more
thorough removal of the silver from the work lead by the
production of a concentration product that is richer in silver
(containing as much as 12 per cent. of silver), and by a higher
yield of silver. The third process, due to Rössler and Edelmann,
consists in adding a small quantity of aluminium to the zinc,
which is used as in the Parkes process.   A very rich silver-zinc
alloy (with 25 to 35 per cent. of silver is thus formed, and is
treated by electrolysis for the extraction of the silver).   (See
Section 3.)

The richest sorts of work lead, and the enriched products of
the Pattinson and Parkes processes are melted in a reverberatory
furnace, and are there exposed freely to the oxidising action of
the air, in the process known as cupellation, until a crude
metallic silver is obtained, lead and most of the impurities
having been removed in combination with oxygen as oxides.
For further purification the metal is refined either by a second
oxidation in a smaller reverberatory furnace, or by melting with
a little silver sulphate in a plumbago crucible.   If the resulting
silver contain gold, it must be further treated by either the
second or third systems.   Experiments have also been made in
the direction of separating argentiferous work-lead directly by
electrolysis.   (See Section 3.)

Amalgamation.—Mercury dissolves silver in considerable
quantities, and can also decompose most of its salts [but not the
chloride] and the sulphide with the separation of metallic silver,
which dissolves in the excess of mercury used.   The silver may
therefore be extracted from ores which contain it either as metal,
certain salts, or pure sulphide, by treatment with mercury,
that is to say, by amalgamation.   The mercury is separated from

the resulting amalgam by distillation, and is thus recovered by condensation, whilst the silver remains behind in the metallic state, but generally alloyed with other metals, such as gold or copper. If it be required to treat other silver ores by this process, the silver must be first converted into chloride by chlorination, or by a chloridising roast [and a reducing agent, such as iron, should be used in conjunction with the mercury]. A large number of amalgamators have been devised for bringing the ore into the most intimate mixture with the mercury, and the more important of them are described in the newer text-books of metallurgy.

The use of electricity in hastening amalgamation has been frequently proposed, but has not come permanently into use. Some of the more important of the patented processes will be referred to in the Chapter on *Gold*, for the extraction of which metal they were originally devised.

Solution of the Silver in Copper.—When ores containing the precious metals and copper are treated by smelting processes, a part of the silver and most of the gold are liable to pass into the bye-product that contains the copper, and, therefore, under certain circumstances, into the copper itself. Ores containing the precious metals are not thus smelted with copper ores, as they might be with those of lead, in order to obtain the gold and silver alloyed with the copper. Copper products containing the precious metals are treated according to systems (2) and (3).

2. SEPARATION OF THE SILVER BY PROCESSES OF CHEMICAL SOLUTION.

The Ziervogel Process.—The matte smelted from the argentiferous copper ores is so roasted that in the first stage, among other products, copper sulphate is formed, whilst in the second stage (after previous crushing of the roasted matte) a double decomposition takes place between copper sulphate and silver sulphide with the formation of silver sulphate. The latter salt is then extracted from the roasted charge by means of hot water and acid solutions of copper sulphate, and the silver is finally precipitated from the resulting liquors by metallic copper.

The Augustin, Patera, and Kiss Processes.—The ores are submitted to a chloridising roast, and the silver chloride is extracted in the Augustin process by concentrated brine, in the Patera method by sodium thiosulphate solution,* and in the Kiss modification by calcium thiosulphate solution. In the first

* [This salt is still commonly known as *hyposulphite of soda*, but as this term belongs more properly to a different compound altogether, the name which is required by the modern system of nomenclature is adopted in the text.—TRANSLATOR.]

case the silver is precipitated in the metallic state by the use of metallic copper, in the other processes it is obtained as sulphide by the addition of soluble sulphides (Na_2S or $Ca(HS)_2$).

The Russell Process.—Ores which contain silver as metal, sulphide, arsenide, or antimonide are treated with a double thiosulphate of sodium and copper. The silver is precipitated from this solution in the form of sulphide as just described. A choice of methods is available for the extraction of the silver from the sulphide. Thus it may be roasted, and the calcined material (or even the unroasted sulphide itself) may be stirred into contact with metallic lead, and the resulting alloy may be cupelled; or the precipitate may be roasted and then treated with sulphuric acid, so that copper and other metals may pass into solution whilst silver is left as a metal.

Sulphuric Acid Processes.—It was explained above that in treating copper ores containing gold and silver, both these metals would be taken up finally by the melted copper. Whilst in the foregoing processes for separating the metals silver has been brought into solution, it is in this instance to be left in the form of an insoluble residue. The granulated metallic copper is placed in a lead-lined wooden tub, and is there submitted to a current of air passing from below upwards, whilst sulphuric acid is allowed to flow over it intermittently in the opposite direction. Through the action of the air, copper oxide is formed, which then dissolves in the acid and yields a solution of copper sulphate. Meanwhile, silver, gold, and some other impurities are left as an insoluble residue, which, after washing and drying, is converted into a lead-silver alloy with the object of submitting it to cupellation. The sulphuric acid treatment of roasted argentiferous matte was referred to in treating of the Russell process. Such mattes are converted by dead-roasting into copper oxide and metallic silver. If, then, the calcined material be treated with sulphuric acid, the oxides will be for the most part dissolved, whilst the silver will be left untouched. The latter is then treated with metallic lead and cupelled.

The parting processes for silver and gold are briefly described in the Chapter on *Gold.*

3. ELECTROLYSIS.

Early Experiments in the Electrolysis of Silver Solutions.—It is generally understood that silver is one of those metals which may, with the greatest facility, be deposited direct by the electric current in a form convenient for further technical use. The value of the metal caused the attention of metallurgists to be drawn to the electrolytic method of extracting it, even at a time when powerful currents could be produced only with difficulty and at considerable cost. After Cruickshanks, at the

beginning of this century, had shown that silver salts, which were soluble in water, could be decomposed by the current with separation of metallic silver, it was only in the arts of electro-plating and electrotyping that any practical use was made of the discovery. But in spite of that, Becquerel, as early as the year 1835, undertook experiments with the view to assist and to accelerate the treatment of silver, lead, and copper ores with the aid of the electric current. The details of this process are given in the Chapter on *Lead*. The principle of the method, which consisted in displacing comparatively electro-negative metals from their aqueous solution by others of a more electro-positive character, and utilising the current thus generated to hasten other less energetic or less complete reactions, deservedly at tracted much attention at the time. In his work, *Sur la Production des Métaux précieux au Mexique*, Duport remarks as follows on this process :—

"What would be the result of a total failure of the supplies of mercury if the Almaden mines could no longer produce cinna-bar, either by reason of the failure of the workings, or by an irruption of water too great to be checked, or, finally, by the failure of all ore that was worth working—contingencies which, although scarcely probable, are yet possible? The production would then be limited to that of the Carinthian mines, and would be altogether insufficient for current requirements. There would in consequence be a great rise in the price, so great as to be equivalent to a complete failure in the supply of the metal. What then would happen to the silver industry in Mexico?

"A few years since it would have been very difficult to find a satisfactory answer to this question, for at that time the only means known for the extraction of silver from its ores were the ordinary smelting process and amalgamation. At the present time the problem wears a different aspect. . . . I [Duport] had the opportunity of convincing myself of the practicability of applying the electro-chemical process to the Mexican ore, and the experiment was as satisfactory as any practical trial on the large scale could have been, because 4000 kg. [4 tons] of an ore which had been sent to Paris from the most important mining district in Mexico were operated upon. The practicability of the process on a large scale once determined, the problem reduces itself to a comparison of the cost of treatment by the old and the new systems."

Although Becquerel did not fail to recall attention to his experiments—in 1869 he wrote a further communication[*] upon the same—yet the improvement in the results does not appear to have been commensurate with the greater expenditure of labour and the higher cost involved, as compared with those of the processes previously in use. It is also to be remarked that

[*] *Dingler's Polytechnisches Journal*, 1869, vol. cxcii., p. 471.

at the date of the last-named paper, the electric current could be generated by dynamo electric machinery, which, however, was still very imperfect in character.

Since that time many proposals have been made to submit ores containing the precious metals to a direct electrolytic treatment, but so far without effect. Some of these processes are based on theoretically correct principles, and allusion will be made to them in the Chapter on *Gold*, which metal naturally claims priority of interest when it occurs along with silver. The treatment of alloys containing the previous metals has, however, been more successful. This may be accomplished in one of two ways. The alloy to be treated being used as the anode, either the silver is left there as an insoluble residue, whilst the other metals are dissolved; or the silver itself is dissolved from the anode and deposited upon the cathode, leaving the alloyed metals at the positive electrode.

Electrolytic Process Depending upon the Insolubility of Silver at the Anode.—If the silver is to be left undissolved at the anode, the alloy to be treated must not contain any great excess of this metal. These conditions exist (*a*) in the refining of copper (see Chapter on *Copper*); (*b*) in the refining of work-lead (see Chapter on *Lead*); and (*c*) in the treatment of zinc skimmings in the Roessler-Edelmann process (see Chapter on *Zinc*). In all these instances the silver plays no part in the electrolytic process; and there is, therefore, nothing more to be added to what is written in the Chapters on *Copper*, *Lead*, and *Zinc*.

Electrolytic Processes Involving Solution of Silver at the Anode.—The Refining of Silver Containing Gold.—If silver be present alone, or in conjunction with other soluble metals such as copper, in such quantities that a second (or third) constituent of the alloy (gold, for example) remains in the form of powder at the anode, it is possible to separate the alloyed metals by the solution of the silver, either alone or with the other soluble metal, as the case may be. The simplest possible instance of this is the refining of silver containing gold.

This process is already in use on a large scale at many separating works.* The method of operation in this case differs from some other refining processes, in the circumstance that the silver cannot be separated in the form of a cohesive plate. Silver may be melted together easily and without loss, however, even if it should have been obtained in the form of powder. Attention may, therefore, be devoted entirely to the far more important point of separating the pure metal with the greatest possible rapidity. On account of the relatively high value of the precious metals it is of the greatest importance that they

* [About 10 million ounces of silver were refined electrically in 1895 in the United States alone.—TRANSLATOR.]

shall not remain locked up in the depositing plant longer than necessary. The current density to be used should, therefore, be as high as is consistent with the avoidance of unnecessary heating of the electrolyte, and with the retention of the impurities at the anode or in the solution. The growth of the silver crystals, which are formed at the cathode when these high current densities are applied, and the consequent possibility of short-circuiting, must be prevented by intermittently or continuously breaking the crystals off the surface of the electrode. The first to recognise these requirements, and to give practical effect to them, was the German Chemist, B. Moebius. The process,[*] which he patented in several countries in the year 1884, was first put into operation in Mexico, and then in the most important separating works in America and Germany with satisfactory results. In Germany the *Deutsche Gold- und Silber-Scheide Anstalt*, which now occupies Roessler's works at Frank-fort-on-Maine, has worked this process, and the following account describes the practice at that installation, which was under the care of Dr. H. Roessler.

The Moebius Process.—As several published accounts have
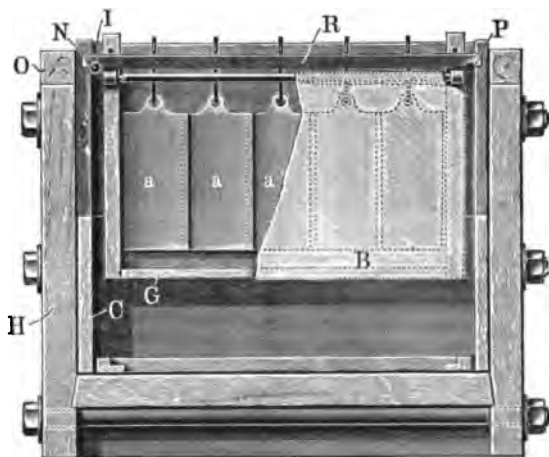
Fig. 133.—The Moebius apparatus, showing anode compartment in half section.

stated,[†] the apparatus has been to some extent simplified

* U.S.A. Patent 310,302 and 310,533, January 6, 1885 ; English Patent 16,554, December 16, 1884 ; German Patent 36,610, December 12, 1884.

† Maynard, in the *Engineering and Mining Journal* (New York), 1891, vol. li., p. 556 ; Roessler, in the *Oesterr. Zeitschrift für Berg- und Hütten-wesen*, 1892, p. 238 ; Schnabel, *Handbuch der Metallhüttenkunde*, vol. i., 1894.
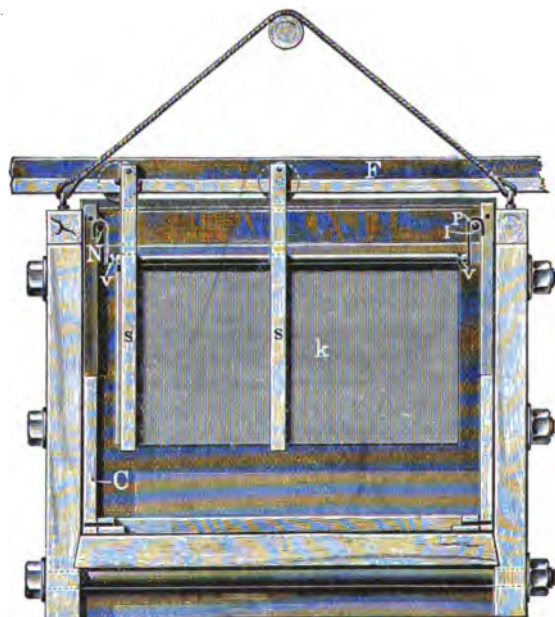
Fig. 134.—The Moebius apparatus—section showing cathode.
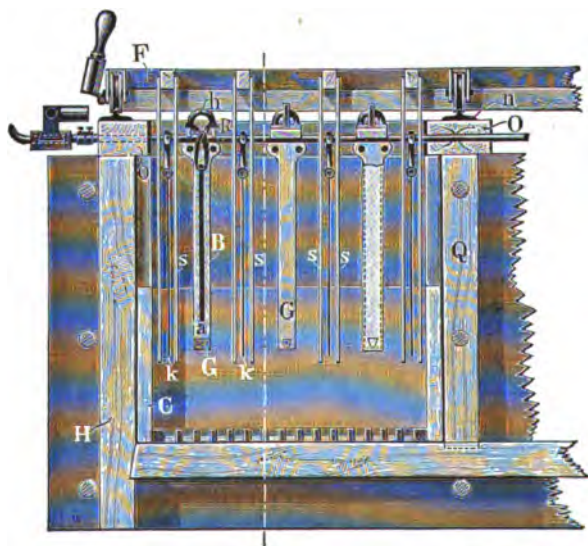
Fig. 135.—The Moebius apparatus—section through A R C E (Fig. 136).

but they do not show any changes in the principle of the apparatus as described in the patent specification.

The electrolyte vats consist at present of long tanks of pitch pine, tarred on the inside about 0·6 metre in width (inside measurement) and 3·75 metre in length [2 ft. × 12 ft.]. Each of these vats is divided by transverse partitions into seven compartments, and every compartment contains three rows of anodes and four cathodes. The anodes are suspended in linen or cotton
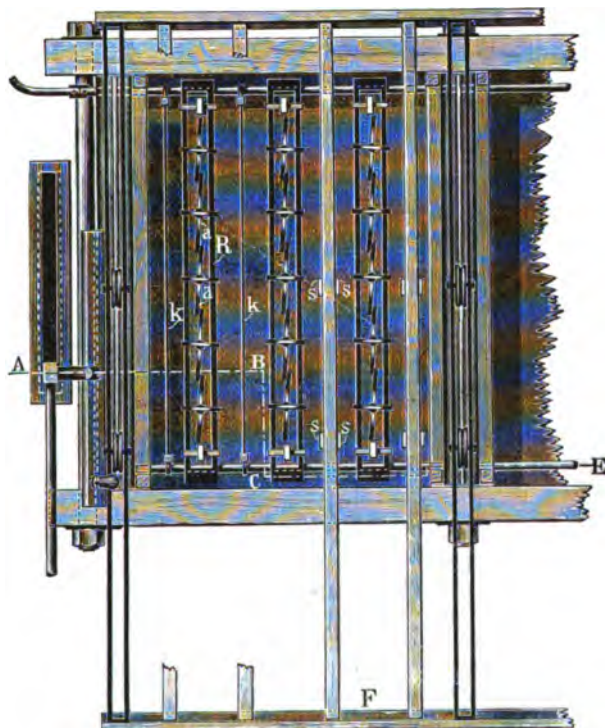
Fig. 136.—The Moebius apparatus—plan.

bags, the cathodes merely hang in the baths. Wooden scrapers are supported from frames, which are free to travel backwards and forwards on the rim of the vat; and these scrapers serve to break off the silver crystals as they grow upon the surface of the cathode, so that all possibility of the current becoming short-circuited is avoided. Under the electrodes, and covering almost the whole floor area of each section of the vat, is a deep tray with a linen bottom, which is intended to receive the principal portion of the crystals detached by the scraper. By means of a

frame, all these arrangements may be lifted together from the vats in which they are suspended. The silver to be refined is cast into anode plates, a (Fig. 133), which are usually 6 to 10 mm. [¼ to ⅜ in.] thick. These are suspended by the double hooks, h, shown in Fig. 135, from a metal frame, R (Figs. 133, 135, 136), which serves both as a support for the plates, and as a means of connection with the current. For the latter purpose, it is placed at one side, in direct contact with the conductor, P, whilst on the other side it is separated from the negative conductor, N, by the insulating sheath, I. In order to prevent the undissolved gold, which is left at the anodes in the form of a brown powder, from mingling with the silver brushed from the cathodes, the anodes are enclosed in bags of closely woven filter cloth, which are stretched on the wooden support, G (Figs. 133, 135); and this in turn is suspended from the frame, R.

The cathodes, k, consist of thin rolled silver plates, soldered to a copper rod, which is suspended in a horizontal position.
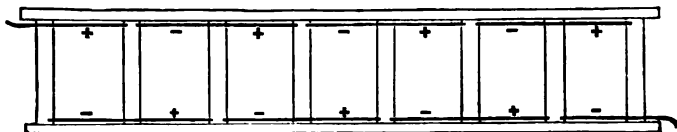
Fig. 137.—The Moebius apparatus—scheme of electrical connections.

At each end of this rod, where it projects beyond the edges of the silver plate, is attached a supporting-hook, v, which serves to suspend the cathode from the positive (P) and negative (N) conductors of the bath; the hook on the one side is therefore placed in direct metallic connection with the negative lead, N, but that on the other side is insulated from the positive conductor, P, as shown in Fig. 134. The advantage of this arrangement is that both conductors are made available as supports, while only one is used to convey the current.

The conductors, P (+) and N (−), are thick copper, brass, or bronze rods; and these rods must not only be thick enough to carry the required current, but they must obviously be capable also of bearing the weight of the electrodes and their supports. The several sections of the vat, usually seven in number, are electrically coupled in series, as shown in the scheme of connections sketched in Fig. 137.

The arrangement of the scrapers, s, is shown in Figs. 134, 135, and 136; they are simply wooden slats, of which two pairs are provided for each cathode plate. They are forked, so as to embrace the cathodes from above, and are supported by the frame, F, shaped like a grid-iron, by which the necessary reciprocating motion is imparted to them. The frame is supported on rollers, which run over the rails, n, these being securely

fastened to stringers forming part of the framework, O, of the top of the vat. The frame is moved to and fro by means of a sliding cam-rail, which is attached to one of the short sides of the vat, and to which a reciprocating motion is imparted by an eccentric. The attachment between them is made by a hinged pin on the frame, which engages with a socket in the slide-bar. The frame, O, together with all parts of the apparatus that dip into the bath, may be raised at one operation by the lifting arrangement indicated in Fig. 134.

The flat wooden boxes, C, serve as collecting trays for the muddy deposit of silver. They are so made that they may be lowered with sufficient clearance, one into each of the compartments of the vat. Thin strips of wood are attached to the sides of the tray, and, being extended upwards, are fastened to the electrode frame, so that the whole may be lifted out of the bath together. The bottom of the tray consists of a grid of laths, fastened by pins, dowelled into the wooden sides of the tray. Before starting the electrolysis, this grid is covered with coarse filtering cloth or sacking, in order that the silver crystals may be retained in it when the tray is raised from the vat. By knocking out the connecting-pins, the bottom may be at once detached from the sides of the tray when it has received its charge of silver and after removal from the vat.

The baths are filled with a weak acidulated solution of silver nitrate as electrolyte, or, if desired, the work may be begun with very dilute nitric acid. As soon as the above described apparatus has been placed in the bath the electrical connections may be completed. The maintenance of a constant current density is of far less importance in this process than in most electrolytic operations. Especially at the outset, or so long as the solution contains but little copper, a very high current density is permissible; it may exceed 300 amperes per sq. metre [0·2 ampere per sq. in.]. In course of electrolysis the copper from the anode (which may frequently contain only 95 per cent. of silver) gradually accumulates in the bath, so that the proportion of copper present will, on the average, be higher than that of silver. The former may amount to about 4 per cent., and the latter to 0·5 per cent., when from 0·1 to 1 per cent. of free nitric acid are present. It is essential that as the percentage of copper increases the proportion of nitric acid be also raised; the current density should be lowered to about 200 amperes per sq. metre [0·13 ampere per sq. in.]. The electromotive force required will usually vary from 1·4 to 1·5 volts per cell. In each of the compartments shown in Figs. 133 to 137 a current of 150 amperes (with an available cathode area of 0·75 sq. metre, or 8 sq. ft.) should suffice to transfer 21·6 kg. [47½ lbs.] of silver from the anode to the cathode in 36 hours. Now, if three rows, each with five anodes of the above-named dimensions, be suspended in the baths, about 1·5

kg. [3·3 lbs.] of silver will be dissolved from every anode plate (or, in other words, almost the whole of the silver introduced will have been carried over to the cathode) in the time quoted. It is, therefore, possible to treat quite considerable quantities of silver within a small area; moreover, the metal is only locked up in the apparatus for a short time, which is a very important consideration in dealing with the precious metals. The cost of the process is not high, as may be easily calculated from the data given above; the separation of gold is practically complete; and, finally, the operation is conducted without any evolution of gas. In spite of the high current density, the heating of the solution is very slight, thanks to the high electrical conductance of the electrode and electrolyte, and especially to the constant movement of the solution caused by the motion of the scrapers.

At intervals of 24 hours the whole of the apparatus suspended in the bath, including the silver trays, should be lifted out by means of its supporting frame. After allowing the trays to drain into the bath they are separated from the electrode frames and taken to the washing plant in order that they may be emptied of silver deposit. This emptying is done, as already indicated, by removing the pins which hold the bottom grids and the filtering cloth to the sides of the trays. The silver is washed, pressed by hydraulic power, dried, and melted together. The anode cells are emptied once or twice a week, according to the proportion of gold in the silver that is being refined. The further treatment of the anode deposit will depend upon its composition. (See *Gold.*)

[The Pennsylvania Lead Company's Plant.—This Company have had the Moebius process in operation at their Pittsburg Works since 1886, and a valuable account of their present practice has been given by Faunce.* It is stated that there are 14 tanks, each of which is divided into seven separate electrolyte cells, but that they are not all in constant use. The details of the plant are similar in most respects to those of the Frankfurt installation. The current density used is 0·125 amp. per sq. in. of cathode surface, and with a solution of silver and copper nitrate containing ½ to 1 per cent. of free nitric acid, and a space of about 1¼ in. between the electrodes, it is reckoned that each kilogramme of silver deposited requires about ⅔ H.P.-hour; in other words, 80 oz. of silver is the equivalent of 1 H.P.-hour. The average outturn of 70 baths amounts to 33,000 oz. per diem, and the metal (which before use has been refined by cupellation until it contains less than 2 per cent. in all of lead, copper, bismuth, and other impurities) is so far purified by the electrolytic process that the crystals, when run into ingots, afford a metal 999 to 999¼ fine.† The anode slimes, after being

* [*Journ. Franklin Instit.*, 1895, and *Mineral Industries*, 1895, vol. iv., p. 355.]   † [99·9 to 99·95 per cent. of silver.]

granulated and parted, yield gold that should be 996 to 998 fine. When the proportion of copper in the electrolyte rises much above 4 to 5 per cent. the solution must be run off from the vats and purified to remove the copper and lead that it contains. But little copper should be present in the anodes, as otherwise this metal would tend to be deposited with the silver. The cost of labour in the process is comparatively slight, a staff of three men by day and one by night sufficing for the whole of the work in connection with the management of the plant, as well as for the melting of the silver and the refining of the gold. In addition to these hands a carpenter is employed daily in repairing and renewing the tanks (about one-seventh of the whole number being always thrown out of use for repairs), and a mason and a machinist are also required about one day a week for general work.—TRANSLATÓR.]
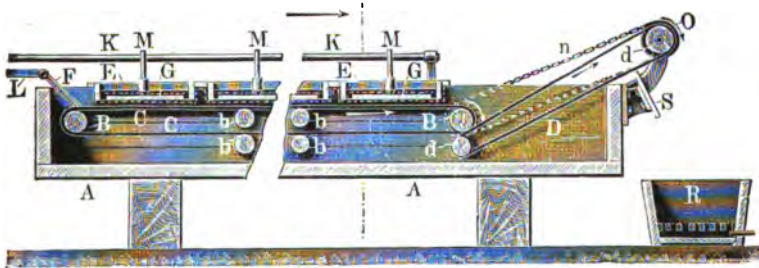
Fig. 138.—The Moebius process ; later form of apparatus.
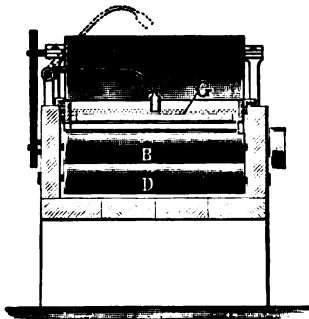
Fig. 139. – The Moebius process ; later form of apparatus.
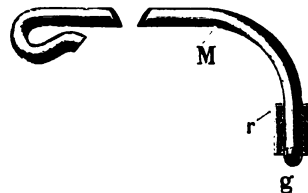
Fig. 140. – The Moebius anode connection (new form).

Later Form of Moebius Apparatus.—In a newer form of apparatus,* shown in Figs. 138, 139, and 140, Moebius has

* [English Patent 469, Jan. 8, 1895, and U.S.A. Patent 532,209, Jan. 8, 1895.]

arranged that the silver shall be deposited upon an endless band
of sheet-silver, C [$\frac{1}{33}$ in. thick], which constantly travels over
the rollers, B, b, in the direction indicated by the arrows in
Fig. 138.   From this moving cathode plate the deposited silver
is carried out of the tank, A, by the conveyor-belt, D, and
delivered into the vessel, R, with the aid of the scraper, S.   The
rollers are actuated by a pulley outside the vat and the chain-
belt, n O.   Within the frame, E, are the anodes, G, of gold-
bearing silver placed upon a permeable support of densely-
woven filter cloth, or of porous clay or the like.   The electrical
connection between the anodes and the conductor, K, is effected
by the wires, M.   These wires (compare Fig. 140) are made of
copper with a platinum cap, g, beneath, any other portion of the
wires that will be immersed in the bath being protected by
caoutchouc sleeves, r.   The brush, F, is used to make contact
between the negative conductor, L, and the cathode, C.   An
aqueous solution of potassium nitrate, acidified with nitric or
sulphuric acid, is employed as electrolyte; and care must be
taken that the liquid is always sufficiently acid, and that it
contains neither too much copper nor too little silver.

[The Perth-Amboy Installation.—The Guggenheim Smelting
Company (of whose installation of the Thofehrn copper process
an account has been given above) have erected an improved
Moebius plant, similar in the main to that just described, at
their works in Perth Amboy, New Jersey.   There are 48
electrolytic tanks,* forming eight groups of six each.   Each tank
is about 14 ft. 3 in. long, by 16 in. wide, by 7 in. high, and is
made of pitch-pine, coated with acid-proof paint.   In order to
economise floor space the tanks are placed in three tiers, one
above the other, with a space of 1 ft. 6 in. between each pair,
the top of the uppermost tank being 5 ft. 6 in. from the floor
level.   Every group of three superposed tanks is separated from
the remaining three of the series by a floor space of 1 ft. 3 in.,
and from the nearest group of another series by 4 ft.   The
cement floor of the building slopes to a collecting pit 30 ft. long
by 4 ft. by 4 ft., in which is a tank for the preparation of the
electrolyte.   The latter should contain 4 to 5 per cent. of
copper, with about 12 oz. of silver per cubic foot (0·13 per cent.),
and about 0·1 per cent. of free nitric acid.   As the electrolysis
proceeds, this free nitric acid becomes gradually neutralised by
copper from the anode, which copper passes into the solution
without being deposited at the cathode.   Fresh nitric acid is,
therefore, added from time to time to maintain the normal
acidity; those anodes which contain most copper requiring the
use of most acid.   On an average it is found that 1½ lbs. of
acid (1·35 sp. gr.) is necessary for each 1000 oz. of doré silver

* [This note is taken from the account in the *Mineral Industry*, 1895,
vol. iv., p. 356.]

treated. The lead in the electrolyte is removed by the addition of a little sulphuric acid at intervals to the solution in the collecting tank, whilst about once in four months a portion of the liquid is replaced by fresh liquor to prevent undue enrichment as to copper.

In each tank there are six frames (E, Fig. 138), 18 in. by 18 in. by 1 in. with muslin diaphragms, and every frame is so divided as to hold four anodes in separate compartments, the anodes measuring 15 in. by $3\frac{1}{2}$ in. by $\frac{1}{4}$ in. each, and being composed of silver doré 980 fine, containing $0\cdot3$ to $0\cdot8$ per cent. of gold. The silver cathode belt is 31 ft. long by 15 in. wide, and is coated once a fortnight on the outer surface with a graphite composition, to prevent the firm adhesion of the deposited crystals. The belt travels at the rate of 3 ft. per minute, the rollers being made of gutta-percha. The electrolyte is circulated through each group of tanks by gravity, ultimately flowing back into the collecting reservoir, from which it is pumped into a distributing-tank at a higher level after it has been made up to the right composition for use.

The generating plant is larger than is required for present needs, but is now producing 220 amperes at 90 volts and depositing 24,000 oz. of silver *per diem.* The tanks are connected in series, each requiring a pressure of $1\frac{1}{2}$ to 2 volts; and each receiving a deposit of 660 to 700 oz. of silver per 24 hours. Exclusive of engine and dynamo, the prime cost of the plant necessary to treat 30,000 oz. of silver doré a day is estimated at $6000, and the cost of refining is reckoned at present to be about $\frac{1}{3}$c. ($\frac{1}{16}$d.) per oz., including the materials, interest, fuel, &c., and the services of three men by day and two by night and of one melter (each at $2.25 *per diem*), but excluding general charges, superintendence, and royalty. A detailed estimate is given, but is not reproduced here, as the figures are not yet considered to be perfectly reliable, owing to the short time that the process has been in operation.—TRANSLATOR.]

The House-Symon Process.—Another form of apparatus has been introduced by House, House & Symon,* but nothing is known concerning its use excepting the statements of the patent specifications. At the present low price of silver the further introduction even of the approved Moebius apparatus, to say nothing of new modifications, is not without its difficulties. The new arrangement offers no simplification of connections or of the moving parts, as compared with the older type, and it will therefore suffice here to give references to the patent specification.

The Separation of Copper-Silver-Gold Alloys.—Alloys containing the precious metals, together with about 60 per cent.

* English Patent 16,002, August 22, 1884. [See *Journ. Soc. Chem. Ind.*, 1894, vol. xiii., p. 1068.]

of copper, are obtained by melting down old gilt and silver-plated ware and the scrap from the working of gold. Hitherto these alloys have been (and even now are for the most part) treated by Roessler's process. The granulated metal is melted with sulphur, so that it may be first separated into cuprous sulphide containing silver, and silver alloyed with gold. The author has had considerable experience with the electrolytic treatment of such material, and he gave an account of the experiments in 1893.*

In order to apply the above-described Moebius process to the separation and immediate re-deposition of silver, either from insoluble metals or from metals which are less readily precipitated than itself, it would be necessary that the insoluble metals present should form but a small proportion of the whole anode, because it is essential that on the solution of the silver from the surface of the anode, the cohesion of the residual matter should be completely destroyed, and the residue itself should be detached from the anode in the shape of a loose powder. These conditions must always be aimed at, not only in the treatment of the rich silver alloys by the Moebius process, but in that of copper alloys by a system of electrolytic refining. In either case a dense cohesive residue, whether metallic, and therefore of high conductance, or non-metallic, and of low conductance, can only be prejudicial to the progress of the work.

If, therefore, adopting the copper refining process as the basis of the separation, the alloy be made the anode in an electrolyte of copper sulphate, copper alone will pass into solution. But the insoluble metals will remain on the surface in comparatively dense, although somewhat brittle and easily crumbled, masses. Some metal slime will, it is true, sink to the bottom of the vat, but it will also happen that fragments broken off from, or flakes still attached to, the anode will fall or lean over against the cathode, and so cause a short circuit. These fragments may be detached, or even broken off by gentle blows, but only so long as the anode plates are comparatively thick. Then, again, on account of the longer adhesion of the fragments to some parts of the plate than to others the anodes are dissolved irregularly, some portions being much thinner than the remainder, so that there is a great risk of large detached pieces of unaltered alloy finding their way into the residue. This irregular solution of the plates producing unequal thickness necessarily leads also to the premature disintegration of the mass. The frequent presence of comparatively large fragments of the original alloy in the residue at the end of the operation causes as much trouble and expense in treating it as if another method of separating the alloy had been adopted from the first.

For the alloys under discussion, therefore, an electrolyte must

* *Berg- und Hüttenmännische Zeitung*, 1893, pp. 251, 269.

be selected which shall effect the solution of silver as well as of copper at the anode. In this case the quantity of residue, which consists for the most part of gold, will almost always be so far reduced in quantity that the required conditions will be fulfilled. Otherwise, the alloy must be remelted with so much copper that the proportion of gold in the resulting material shall not exceed 20 per cent., while it is better that it should fall below 15 per cent.

Borchers' Apparatus. — The alloy should be granulated before treatment. The electrolyte may be either dilute nitric acid or an aqueous solution of nitrates, among which copper nitrate is the most suitable. The form of the apparatus to be used depends upon the nature of the residual gold, which may consist of a heavy powder, of flocculent masses, or even of very fine metallic particles that may remain mechanically suspended in the electrolyte. In all three cases the residue is easily detached from the portion of the anode not yet attacked; and its separation, therefore, offers but little difficulty, as will be understood from the following description of the method of using the apparatus illustrated in Figs. 141 to 144.

This arrangement is adapted for use with products which deposit a

Fig. 141.   Fig. 142.

Borchers' electrolytic cell for the treatment of alloys.

relatively heavy insoluble residue. It is well known that only those bodies will sink through an ascending current of water which are capable of sinking through still water with a velocity greater than that of the current to which they are exposed. All other bodies are either held in suspension or are carried along by the current. In these two figures, *g* is the electrolysis vessel, in which is inserted a cell, *d*, provided with perforated double walls at the sides. This cell runs the whole length of the outer vessel, and therefore divides it into three compartments, the inner cathode cell, *k*, and the two outer anode spaces, *a*. The prismatic trough, *g*, terminates below in

a spitzkasten* or pointed box, with an inclined channel and exit pipe, r.

The anode compartments, a, are filled with granulated alloy. The electrolyte flows into the cathode cell, k, within which the metal is deposited upon a suspended metal plate. The bulk of the solution flows through the tube, s, into the spitzkasten below, and hence rises into the anode compartment above. The heavy particles of residual matter remaining from the decomposition of the anodes sink through the ascending current of liquid and, finding their way through a layer of coarse spheres made of non-conducting material with polished surfaces, remain at the bottom of the trough; they are run off through the opening below, either continuously or from time to time, and are accompanied by a small proportion of liquid. The electric current is conducted to the granulated anode metal through jointed rods of the same alloy as the anode itself. Each rod terminates at one end in a point, and at the other it has a corresponding socket. The conducting connections are dissolved simultaneously with the rest of the material; but that is no disadvantage in this case, because another length of rod may be inserted into one that is dissolving away and is sinking deeper into the trough. The top joint of this compound rod is connected to the conducting cable by means of a point of the same shape as those used for the alloy-rods. The hollow space between the double walls, d, of the cathode cell is filled up with a filtering medium, which should be so dense that only a small quantity of liquid may penetrate. through it, although it allows the electric current to pass freely. The electrolyte, after flowing through the cathode- and anode-compartments, enters above the inner and lower rim at the top of the vessel, g, into a channel through which it is carried off to be treated (in some cases, after filtration) for the precipitation of one or other of its constituents, prior to its return to the cathode cell of the same or of a similar vat.

Another form of the apparatus is shown in Figs. 143 and 144. It has the advantage that the layers of anode material are not so high as in the previous type, so that the lower portions of the granulated metal are not subjected to premature disintegration or to pressure. However, this form allows of a considerably higher current density at the anode, owing to the extended cathode area, as compared with the older cell; and the work of solution progresses, therefore, to a corresponding extent more rapidly. Finally, the partial separation of various relatively heavy constituents may be effected. In this case only one anode chamber, a, is provided for each electrolysis tank, g; it is shown in the figures to the left of the cathode compartment, k. The partition

* [The *Spitzkasten* is a special form of washing apparatus used in the dressing of fine-crushed ores for the separating of certain heavy constituents from the remainder by means of a stream of running water.—TRANSLATOR].

separating the two sections of the vat is so made that only the electric current may pass through it, as in the previous plant.
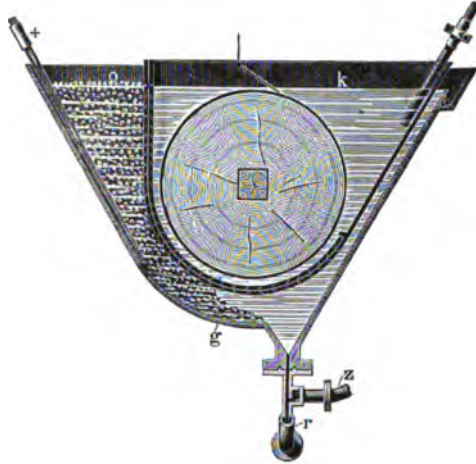
Fig. 143.—Borchers' modified electrolytic cell
for the treatment of alloys.
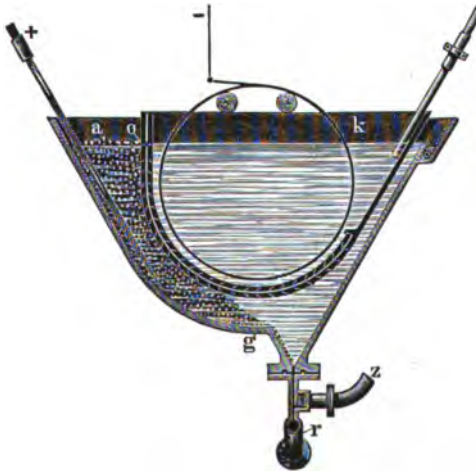
Fig. 144.—Borchers' modified electrolytic cell
for the treatment of alloys.

The cathode is placed in a wide compartment, and consists of a hollow cylinder of sheet-metal bent over a wooden roller (Fig. 143) that can be rotated from without; or, the core being omitted,

it may be rotated by two narrow rollers placed above the liquid as shown in Fig. 144. Connection is made with the negative conductor by the brushes placed above, these being pressed against the surface by a spring. The electrolyte is introduced into the cathode compartment, where the metal is deposited on the surface of the revolving cathode; it then passes through a series of openings, o, into the anode compartment, and, flowing first downwards, and circulating among the granules of the alloy, it finally rises again into the free space to the right. This flow of solution carries down with it all the insoluble residue washed off the surface of the anode granulations. A current of liquid is caused to enter the contracted well, g, at the bottom of the vat through a long and narrow slot, and this liquid mingles with the electrolyte, and so increases the rate at which it travels upwards through the right-hand portion of the vat. By regulating this rate of flow it is possible to effect a separation of the light from the heavy particles of the residue in suspension. The heavier portion of the slime escapes through the slot and the tube, r, which is connected with it as in the apparatus previously described. The solution that is admitted mechanically to assist the separation enters the slot by the tube, z. The electrolyte, after passing through the vat, overflows through a channel above, exactly as shown in Figs. 141 and 142. After filtering the saturated solution, and, if necessary, separating some of the dissolved constituents, it is returned to the cathode cells where the metal that is most easily separated electrolytically from the remainder will be deposited.

The author has treated ores and smelting products containing the precious metals, with apparatus of the type just described, but put together in the most primitive manner from scrap and lumber; and yet the results were quite satisfactory. The experiments were made in an American factory, and extended over some ten years. A properly constructed apparatus was then put together, but was not used on account of the author's return to Germany.

The Dietzel Apparatus.—An apparatus patented by Dietzel[*] for the same purpose is based to some extent on the same idea. A vat with a bottom, sloping either towards the middle or to one side, is lined with carbon plates, on which the granulated metal to be treated is gradually moved downwards with the aid of suitable mechanism. The cathodes, which are suspended in the copper nitrate electrolyte, consist of straight copper plates or of sheet copper, bent over wooden cores into cylinders, and are enclosed within open wooden vats, of which the bottoms are formed of a dense filtering medium, such as linen. These vats must be of sufficient size to allow ample room for the introduction and movement of the grains of alloy. The latter is con-

[*] German Patent 68,990.

nected, as the anode in the circuit, by contact with plates of conducting, but not soluble, material at the bottom of the bath. The circulation of the electrolyte and the progress of the operation is as follows :—

(1) Introduction into the cathode compartment, with separation of copper. (2) Penetration through the filter at the bottom of the cathode cell into the space around the anode, where copper and silver are dissolved, and gold is left as a residue. (3) Transfer to the filtering and precipitating plant, where any gold previously held in suspension is caught, and silver is precipitated by means of copper. (4) Re-introduction of the copper nitrate solution into the cathode compartment.

Since the plates to be employed in making connection between the positive lead, and the anode must be "conductant but insoluble," it will be remarked that carbon is not here available. It is well known that carbon plates have but a short existence under the influence of such high current densities as are necessary [for economic reasons] in the treatment of valuable raw materials. In this case the ordinary disintegration of the plates would be greatly hastened by the mechanical action of the grains of alloy as they slowly move over the surface of the carbon. No doubt the mere consumption of carbon would not be a very heavy charge, taking into account the value of the metal under treatment, for even the best carbon plates in these days are not costly. But the carbon powder resulting from the disintegration of the plates would mix with the pulverulent gold residue from the anodes in such quantities, that the separation of the two materials would prove to be a more difficult problem even than the separation of the original alloy components.

In a newer modification of this apparatus, described in a private communication written by Dr. Dietzel to the author, the platinum wires, P (Fig. 145), are substituted for carbon plates.

In order to accomplish the introduction and movement of the alloy, S, beneath the diaphragm, D, more conveniently (especially in certain cases, such as the treatment of large quantities of base alloys), the vat, which is constructed in the shape of an inverted roof, or with an otherwise sloping bottom, is made as elongated as possible, and the support for the alloy, S, is provided with rollers, r, which run on the rail, s. In this way it is possible to convey the residual slime from the treatment of the alloy to openings at the ends of the long sides of the vat, or to introduce fresh material in the same way.

The composition of the raw material may average 55 per cent. of copper, 36 per cent. of silver, and $5\frac{1}{2}$ per cent. of gold, together with some zinc, lead, tin, nickel, cobalt, iron, manganese, aluminium, platinum, &c. The alloy is cast into plates, S, about 3 to 4 mm. [$\frac{1}{8}$ in.] thick, which are then laid upon the platinum

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wire conductors.   The electrolyte consists of a slightly acid
solution of copper nitrate, with 3 to 5 per cent. of copper and
small quantities of free acid.   On the admission of the liquors
into the cathode compartment, the proportion of free acid should
be at least 0·1 per cent ; but should not exceed 0·2 to 0·4 per
cent. at most.   This proportion may be regulated by the addi-
tion, as required, of a strongly acid solution of silver and copper,
which is obtained from the treatment of the gold slimes with
boiling nitric acid.

The form of the diaphragm, D, remains practically the same as
that originally adopted.   As already indicated, the diaphragm
itself consists of close linen cloth stretched obliquely across the
bottom of the cathode compartment.   The slanting position is
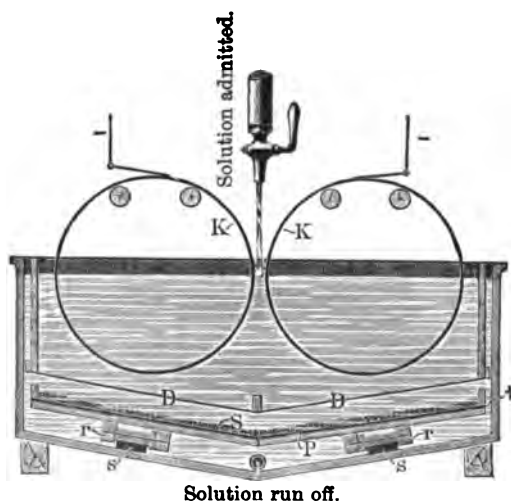
Fig. 145.—Dietzel's alloy-separating vat.

adopted, because after the bulk of the silver and copper have
been dissolved from the anode material, a considerable quantity
of oxygen is necessarily generated in contact with the insoluble
residue, owing to the high current density used ; and this oxygen
must of course be conducted freely away from the cathode cell.
The cathodes consist of rotating copper cylinders, K, the surface
of which is coated with a thin layer of graphite, so that the
electrolytic copper may be readily stripped from it, as soon as it
has been deposited to a sufficient thickness.

The methods used in conducting the operations remain un-
altered.   Many details, no doubt, require further development,
as in the case of all new processes.   But over a ton of metal has
already been separated in this manner.

A number of other methods, which have been brought forward for the extraction of the precious metals, will be discussed in the next chapter, at least, so far as they are founded upon practicable ideas.

Applications of Silver.—Silver is not very extensively used in the pure condition on account of its inferior strength. Excepting, therefore, for the production of pure compounds of silver, which are very largely employed, especially in photography, and for scientific instruments, chemical apparatus, and silver-plated articles, it is almost always alloyed with copper. These alloys, which contain up to 90 per cent. of silver,* are very generally used for coinage purposes, and for the production of household implements and objects of art, or silversmith's work.

CHAPTER III.

GOLD.

Properties of the Metal.—Gold (Au; atomic weight = 197; specific gravity = 19·3) is a yellow metal with a brilliant lustre; it is strong, and is the most malleable of all metals. On account of its softness and its other mechanical properties a fractured surface shows no appreciable crystalline structure, but appears hackly. Gold melts at a temperature of 1035° C., and at about 2000° C. it begins to vaporise. Its conductance in respect of heat and electricity is very high, and may be represented by the numbers 60 and 70 respectively, if the conductance of silver be regarded as 100. The tendency of gold to absorb gases when in the molten condition is very small as compared with that of silver. On the other hand, the solid metal, when in the finely divided condition, is capable of condensing about 0·7 per cent. of electro-positive gases (H, CO, &c.). In its power of dissolving or being dissolved by other metals it is very similar to silver. The alloys of these metals, particularly those with lead, mercury, copper, and zinc, and the alloy of gold with silver, have a special interest for metallurgists. The presence of a very small proportion of foreign matter (0·05 per cent. of lead, bismuth, or tin; or 0·00003 per cent. of antimony) suffices to destroy the malleability of gold and to make the metal weak and brittle.

In its chemical aspect, gold is one of the most stable of metals. Its oxides and sulphides can only be produced indirectly, and are very easily decomposed. Halogens, especially chlorine and

* [The foreign silver currency contains 90 per cent. of silver. In England the standard alloy for coinage and plate contains 92¼ per cent. of silver and 7½ per cent. of copper.—TRANSLATOR.]

bromine, and mixtures (like *aqua regia*) which evolve these elements, attack gold readily. Certain salts, such as the thiosulphates and cyanides, may form with metallic gold double salts that are soluble in water ($3Na_2S_2O_3 + AuS_2O_3 + 4H_2O$; and $AuCy . KCy$); but the cyanides require the presence of oxygen to enable them to dissolve gold. By using these salts, therefore, as electrolytes it is possible to dissolve gold at the anode and to reprecipitate it at the cathode. Excepting in the form of thiosulphate, gold does not tend to play the part of base to oxygen acids, but its oxide may act as an acid and form salts, termed aurates, with other bases. Sulphide of gold dissolves readily in solutions of the alkaline sulphides to form thio-salts.

Gold may be precipitated from its solutions by even the weakest reducing agents, and is thus separated in the metallic state through the agency of hydrogen, phosphorus, arsenic, antimony, carbon, by nearly all metals (excepting from cyanide solutions, from which it can only be deposited by zinc and metals more electro-positive than zinc), by metallic sulphides, by the proto-salts of iron, tin, &c., by hypophosphites, sulphites, and sulphur dioxide, by the lower oxides of nitrogen, and by arsenic, oxalic acid, and many organic substances.

Occurrence of Gold in Nature.—In nature gold is distributed over a very wide area, but it is present in only very small proportion in the rocks which contain it. It is found in many veins, rocks, and deposits, but only in a few places in sufficient quantity to repay extraction. It occurs almost exclusively in the metallic state, although usually as an alloy with varying proportions of other metals; it is only known with certainty to be found mineralised in the form of telluride. It is generally present in minute quantities in the ores of copper, lead, and silver.

The extraction of gold from ores, metallurgical products, and waste material or scrap, has been accomplished in various ways viz., by :—

1. Mechanical treatment (washing).
2. Solution in other metals (amalgamation and solution in lead).
3. Purely chemical solution and precipitation.
4. Electrolysis.

1. MECHANICAL TREATMENT.

Washing.—All mechanical processes for treating auriferous materials (natural sands or artificially crushed rocks) are based on the circumstances that, in streams of water flowing in a horizontal direction, the suspended matter which has the highest specific gravity (gold, therefore, before nearly all other materials) will sink first to the bottom, whilst those which are specifically

lighter are carried on in suspension ; and that in currents rising in a vertical direction, only those particles will be held in suspension which in still water would naturally fall with a velocity equal to or less than that of the ascending stream. For the details of the apparatus required for this washing process the reader must be referred to works on ore-dressing and preparation. At the present day these processes are practically used only in conjunction with amalgamation.

2. SOLUTION OF THE GOLD IN OTHER METALS.

Treatment with Lead.—Concerning this method it will suffice to refer to the remarks on the corresponding method of extracting silver. In cases where the system is adopted (and that is, of course, where lead smelting is in operation) the gold ores treated uniformly contain a far larger proportion of silver than of gold. When copper is also present a part of the gold always passes into the copper-bearing products, such as the matte and metallic copper, &c. The concentration of poor work-lead and the process of cupellation have been sufficiently described in the Chapter on *Silver*.

Amalgamation.—It has already been stated that the mechanical preparation of auriferous ores, which mostly contain but little gold, is nearly always a preliminary to the process of **amalgamation or solution of the precious metal in mercury.** Under some circumstances the ore is submitted to an oxidising or chloridising roast before treatment with mercury. In sluice amalgamation the auriferous gravel is washed down by powerful jets of water from the exposed faces of the deposit, and is treated directly with mercury ; but this treatment is forbidden in California, where it had been most used, because the enormous masses of gravel to be disposed of after treatment was causing the silting up of important watercourses. In contrast to the amalgamation of most silver ores and products, in which the silver occurs in chemical combination, the amalgamation of gold ores is practically a simple process of solution, which can usually be accomplished after mere mechanical crushing and concentration. In some cases the amalgamation is begun even during the operation of crushing ; in other cases the mercury is only applied after the material has been reduced to a powder and concentrated by a suitable washing process. Roasting is only effected in a few cases in which the grains of gold are so enclosed that the contact with mercury would be hindered.

3. CHEMICAL PROCESSES OF EXTRACTING GOLD FROM ORES.

Chlorination.—When chlorine acts upon finely divided and moist gold ores, which are free from sulphides, arsenides, and antimonides (or which have been previously roasted if these substances were originally present), a chloride of gold is formed that is readily soluble in water. For the purpose of chlorination the ores, whether raw or roasted, are moistened or suspended in water (**Plattner's process**). The chlorine is produced outside the chlorinating vat, and is then led into the mass of ore in the latter vessel; but in place of using free chlorine the ore may be mixed with substances which are capable of evolving the gas *in situ*, as, for example, sulphuric acid with manganese peroxide and common salt, or with chloride of lime. The chloride of gold is subsequently dissolved by treating the mass with water; and the gold is precipitated from the resulting solution by the addition of ferrous sulphate or soluble sulphides (H_2S, Na_2S, $Ca(HS)_2$), or by filtering through wood charcoal, which reduces and retains the precious metal on its surfaces. In the former case the precipitate of gold is melted with suitable fluxes to remove small quantities of impurities; if necessary it is re-dissolved and re-precipitated prior to this treatment. In the latter case the dried charcoal is burnt off in reverberatories or small blast furnaces, and the gold is recovered as a fused mass which separates easily from the melted ash of the charcoal.

In the chlorination of gold ores, the silver remains as an insoluble chloride in the residue, and may be afterwards extracted by treatment with a solvent, such as brine or thiosulphate solution.

Bromine may be used as a substitute for chlorine in the treatment of gold ores.

Cyanide Extraction Process.—Metallic and mineralised gold are soluble in aqueous solutions of potassium cyanide. Oxygen is necessary to the solution of metallic gold in this way as Elsner [*] showed nearly 50 years ago—

$$Au_2 + 4KCy + O + H_2O = 2KCy . AuCy + 2KOH.$$
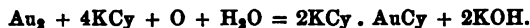
The assertion of MacArthur and Forrest to the contrary is erroneous, and in this sense their patented process cannot be considered as new. Elsner's statement is confirmed by later observations, according to which the addition of an oxidising agent (such as sodium peroxide or potassium ferricyanide) accelerates the solution of the gold. In practice the ores are extracted, first with dilute solutions of potassium cyanide (0·8 to 0·2 per cent. of KCy) and then with water. The gold is

* Elsner, *Journ. für prakt. Chem.*, 1846, vol. xxxvii., p. 333.

obtained from the resulting solution by precipitation with zinc or aluminium, or, more recently, by electrolysis. (See Section 4 of this Chapter.)

Removal of the Impurities by Fusion.—This treatment of impurities by oxidation, sulphurising, or chloridising is practically applied only to alloys. To this group belong the cupellation of lead containing the precious metals (see *Silver*); the separation of gold from copper and (latterly only in part) silver by the combination of the two latter with sulphur during a fusion with sulphide of antimony or with sulphur (**Roessler's process**); and, finally, **Miller's process**, used at the Mint in Sydney, consisting of the passage of chlorine through the alloy of gold and silver fused under borax in a clay crucible, by which chloride of silver is formed. In addition to the cupellation process, Roessler's method is used for the treatment of gold-silver- and copper-, and Miller's for the treatment of gold-silver, alloys.

Solution of the Impurities in Acids.—This process may also be used for alloys. The oldest process of all, that of **quartation**, or **inquartation**, in which the silver of the alloy is separated from the gold by solution in nitric acid is used only in most exceptional cases outside the assay-laboratory. At the present time, if electrolysis is not to be applied, the **sulphuric acid separation process** is used. The granulated alloy is heated with strong sulphuric acid; gold then remains as a brown residue, whilst silver is converted into sulphate, at the expense of a portion of the sulphuric acid. The washed residue is dissolved in *aqua regia*, precipitated by means of a ferrous salt, filtered, washed, melted with suitable fluxes, and cast into bars. The silver sulphate is then decomposed by scrap-iron, the separated silver is washed, pressed, dried, and fused. The separation of the precious metals from copper, by treating the alloy with **sulphuric acid in an excess of air**, has been described in the Chapter on *Silver;* but the process is superseded in most works by electrolytic treatment.

4. ELECTROLYSIS.

Electrolysis, with Separation of Gold in Insoluble Form at Anode. — As already mentioned in the Chapter on *Silver*, there are many processes practically available, and many of them in actual use, for the *separation of gold and other precious metals* in the insoluble anode residue. Of these the method used in the refining of silver has already been described, and for the others, reference may be made to the Chapters on *Copper, Lead, Zinc,* and *Antimony;* for in all such cases alloys containing the precious metals would be under treatment, and the above-named metals, rather than gold, would play an active part in the electrolysis.

Electrolysis with Solution and subsequent Deposition of Gold.—Gold forms no exception to the general rule that, if it is to be brought into solution electrolytically, it must either be used as anode, or be brought into the closest possible proximity to an anode at which are liberated anions capable of dissolving it. It has been said that the solvents for gold are solutions containing chlorine, and those of potassium cyanide to which oxygen has access. These conditions appear simple enough, and are, indeed, easily fulfilled, when alloys rich in gold are to be treated. B. Bock,[*] in 1880, described a process used for the separation of gold containing platinum at the North German Refinery in Hamburg.

(a) **Treatment of Gold containing Platinum.**—"A number of the gold plates to be treated are suspended from a copper rod in such a way that their whole surfaces are immersed and form the positive electrode in a dilute solution of chloride of gold contained in a suitable vessel. Very thin plates of rolled fine gold are suspended in a similar way from a second copper rod, and are arranged in the bath alternately with the anode plates. On making the proper electrical connections with the copper rods, the fine gold plates increase in thickness at the expense of the impure sheets. Iridium, osmiridium, and similar metals, being insoluble, separate and fall to the bottom of the bath in the form of greyish-black granules. When the gold plates are sufficiently thick, they are changed, and those which were removed are washed, dried, fused in crucibles, and cast into bars of fine gold."

No details are given of the composition of the alloy that was electrolysed, or of the current density employed, so that it is impossible to estimate whether the progress of the operation is *sufficiently rapid* in view of the high value of the material treated. It has already been shown that for the electrolytic extraction of the precious metals it is not sufficient that the deposit should be pure; it is of the utmost importance that it should be produced quickly. If, however, as was evidently the case in the process last described, the gold is to be obtained adhering to the cathode, the current density used must not be very high. It is true that the deposit need not possess the properties which the electro-plater endeavours to secure, when he employs a current of 20 to 25 amperes per sq. metre [0·013 to 0·014 amp. per sq. in.], but a density of 50 to 60 amperes per sq. metre [0·03 to 0·04 amp. per sq. in.] must not be exceeded, unless the anodes or cathodes be surrounded by cells or filtering media, which shall serve to prevent the residue upon the former from mixing with the refined metal precipitated upon the latter.

Unfortunately, this simple case of gold electrolysis is exceptional. The materials, which it may usually be required to

* *Berg- und Hüttenmännische Zeitung,* 1880, p. 411.

treat by extracting the gold in a soluble form and subsequently precipitating it, contain only a small fraction of 1 per cent. of gold, whilst even in the most favourable cases the whole of the remaining mass consists of finely divided insoluble mineral suspended in water. The first problem to be attacked was the extraction of gold as directly as possible from its more refractory ores; and the earliest experiments in this field were, therefore, . concerned with the electrolysis of ores.

(b) **Electrolysis of Ores.**—At first it was attempted to introduce electrolysis into the process of amalgamation, and, using mercury cathodes, to electrolyse solutions in which the ore had been suspended. Such an arrangement may be of assistance in two ways—First, it might be expected that the very light particles of float-gold (which, by remaining in suspension, would generally fail to be acted upon by the mercury) would be brought into contact with a suitable anode, and thus becoming dissolved would be carried over to, and be deposited upon, the cathode. Secondly, the surface of the mercury which serves as the solvent for gold in an amalgamator should remain cleaner, for the use of the mercury as cathode would check the formation of a pellicle of oxide or sulphide upon it. Nevertheless, the expectations in these respects have not been fulfilled. Before passing, however, to the consideration of the causes which have contributed to the unsuccessful results obtained up to the present, reference may be briefly made to some of the processes which have been tried.

Barker's Process.—The first patent of this nature was that granted to Barker,* from whose specification the following account is taken. The ore to be treated is carried by a stream of water over a series of riffles, which contain mercury connected with the negative pole of an electric generator, and provided with stirrers, beside which the anodes may be arranged :—

" Fig. 148 shows a longitudinal sectional elevation, Fig. 146 a plan, and Fig. 147 details of one part of the apparatus on a larger scale than in the other figures.

" A is a riffle table, in which are formed the riffles, a a a; this table and the riffles may be made in one piece, or otherwise, as may be most convenient. The material I prefer to employ in the construction of my riffle table and riffles is wood, but porcelain, earthenware (glazed or unglazed), or any combination of the above-mentioned materials may be employed. The number of riffles in a table depends upon the nature of the ore to be treated ; where the ore is refractory ten riffles (as shown), or more, may be required.

" In the first series three riffles are shown, each one provided with combined revolving mechanical stirrers and revolving electrodes (anodes), B. Each set of stirrers consists of a shaft, b,

* German Patent 22,619, October 26, 1882. [English Patent 3046, June 28, 1882.]
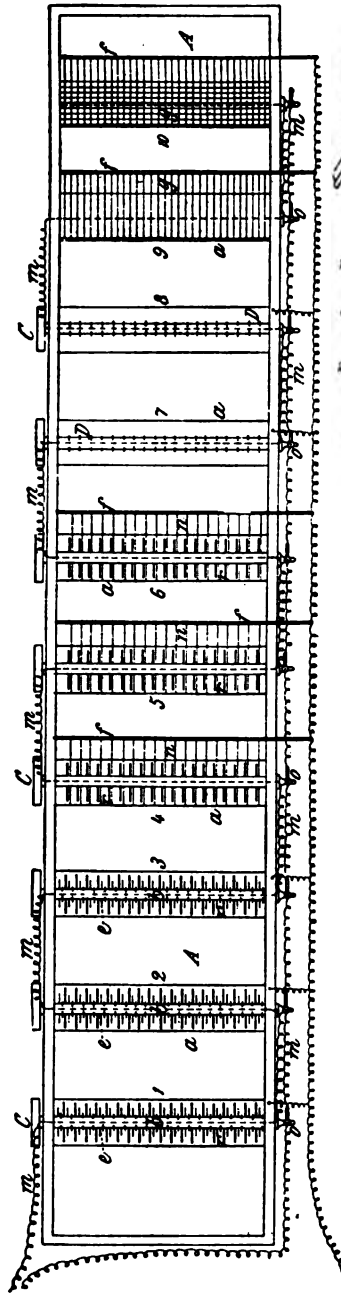
Fig. 146.　　　Fig. 147.　　Fig. 148.
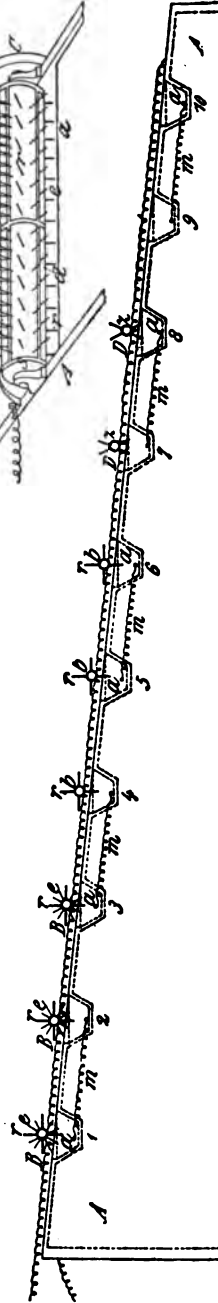
Barker's gold-extraction plant.

to which are attached arms or pins, *r*, which act as the stirrers, and a second set of arms or pins, *e*, which act as electrodes. These shafts are kept in constant contact with the main current of electricity by means of any suitable connection. The mechanical stirrers are designedly longer than the electrodes; the object in making the electrodes shorter than the stirrers is to prevent them from coming into contact with the mercury, which would otherwise destroy the whole operation.

"In the second series, the stirrers are the same as described in the first series, but instead of the electric current being supplied along the shaft, it is conveyed by wires or plates, *n* (Fig. 146), which are laid across the riffle, a little above the mercury, special care being taken that they shall not come into contact with the mercury.

"In the third series, the mechanical stirrers are dispensed with, but the current is rendered intermittent by means of a special construction of revolving electrode, D, and is supplied along the shaft, as in the first series, but in such a manner that when the arms or pins are perpendicular, as in Fig. 148, the current is caused to flow, and, when horizontal, the current is interrupted.

"In both the first and the third series, I establish the electric connection by strips, d_1, and bands, *d*, of metal arranged on the surface of the shaft, as clearly shown in detailed view (Fig. 147), or by a metallic core, in contact with the inner ends of the electrodes.

"The shafts are made of wood, the stirrers of any suitable non-conducting material, and the electrodes (anodes) of brass, or any other hard and durable metal. The shafts may also be made of metal, and where metal is used, the shafts would be insulated in the usual way.

"In the fourth series, I dispense with the shafts and stirrers, and in this instance the electrodes are carried across the riffles either as shown in the ninth riffle in Fig. 146, or interlaced as shown in the tenth riffle.

"In all cases, care must be taken that the electrodes (anodes) shall never come into contact with the mercury (cathodes).

"Each riffle is provided at bottom with a tap or cock, *o*, by means of which the mercury may be drawn off. Or the conducting wire may be passed through the heads of the plugs of the taps or cocks, and when desired to run off the mercury, this wire must be disconnected and removed.

"The electric current is supplied direct to one end of the first riffle, and passing through the mercury, then conveyed or led out by the wire, *m*, to the adjoining riffle, and so on, to the whole series of riffles, as shown in full lines and dotted lines in Fig. 146. The return current to the electric generator in the first and third series is conveyed by depressing screws, suitably placed

for the purpose, on the side of the riffle table, and in immediate proximity to the shafts, so as to come into contact with the metallic bands, d_1, but in the second and fourth series by the bars, ff.

"At that side of the riffle opposite to the discharge taps or cocks, each shaft carries a pulley, C, for the purpose of revolving the same, and the pulleys may be driven by any suitable gearing. The most suitable speed for the shafts is 45 revolutions per minute.

"Mercury is supplied to each riffle in the manner employed in the ordinary amalgamation, and in my invention discharges the duty of a cathode in each riffle. The ore is supplied to the platform at the head of the table in the usual way. The table, A, is placed at a suitable inclination, and a current of water is applied in such a manner that the ore is caused to travel down the table, and pass through each of the riffles between the several sets of electrodes (cathodes and anodes).

"The electric action upon the surface of the mercury keeps the titanic sand, &c., in a constant state of agitation, thereby ensuring perfect contact between the mercury and the particles of gold and silver, which would otherwise be lost, as the titanic sand, &c., would form a layer upon the surface of the mercury, and so cause imperfect amalgamation, with a consequent loss of gold or of silver."

Bonnet's Process.—Bonnet * injects finely divided mercury into a current of water in which the particles of ore are carried in suspension, and through which an electric current is passed.

Body's Process.—Body † uses an iron drum provided with iron balls, after the fashion of a globe crushing mill, and filled with a ferric solution. The powdered ore is introduced into this solution. The axle of the drum is insulated from the drum itself; it is placed horizontal, and is provided with carbon rods, which project into the liquid within. The noble metals become dissolved electrolytically through the agency of the ferric salt, during the revolution of the cylinder, and are deposited on the iron walls and balls which serve as cathodes. Mercury is then introduced into the apparatus to dissolve the free gold and silver.

Molloy's Process.—Molloy's numerous patents, taken out during the years 1884 ‡ to 1887,§ were concerned with the use of the electric current in an apparatus of the type familiar in the old amalgamating mills of Schemnitz. The ore to be treated is

* U.S.A. Patent 298,663, May 13, 1883.
† German Patent 24,876, May 18, 1883. [English Patent, 2390, May 10, 1883.]
‡ German Patent 28,452, January 8, 1884. [English Patent 143, January 1, 1884.]
§ U.S.A. Patent 363,411, May 24, 1887. [English Patent 15,206, November 22, 1886].

introduced into the electrolysis vessel, G (Fig. 149), through the hopper, T, which forms the centre of the plate, B. This plate is bent upwards at the circumference, so that it forms a circular rim ; it may be rotated by means of the spindle, W, to which it is attached by a cross bar, so that it hangs suspended upon a layer of mercury, K, that serves at the same time as solvent for the gold and as cathode for the current. The particles of ore are driven by the stirring mechanism, O, between the mercury and the plate which is tapered off at the part below the hopper ; owing to the rotation of the plate, the particles now take a spiral course over the surface of the mercury until they reach the annular space between the edge of the plate and the wall of the vessel. Here they are kept in motion by the stirrers, o', attached to the circumference of the plate, and they are finally discharged over the outer rim, G. The mercury rests on a dia-
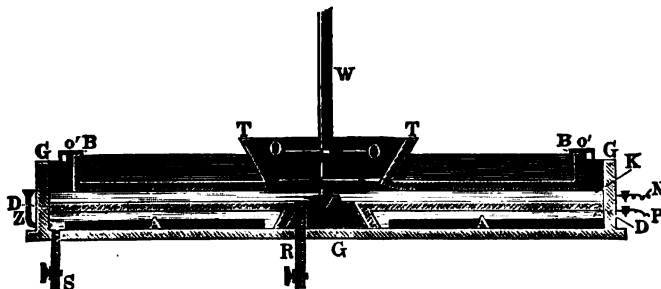
Fig. 149.—The Molloy amalgamating pan.

phragm, D, which is made of clay, cement, leather, wood, from which the resin has been extracted, or other suitable material, and which forms a tight joint both with the outer rim of the vessel and with the socket of the shaft spindle, W. Anodes of carbon or sheet lead, A, are introduced at the bottom of the vessel, G, and the space beween them and the diaphragm, D, is filled up with sand. The tubes, Z and S, serve respectively for the supply and the removal of the electrolyte, which consists of dilute sulphuric acid, of caustic soda, or of sodium salt in solution. Since oxygen is evolved at the anode during the process, the diaphragm must be made to slope slightly from the centre to the circumference, and, at the highest point, an outlet must be provided for the gas. N and P are the conducting wires. The tube R is intended for the removal of the mercury from the cathode compartment.

Modified Forms of Apparatus.—The forms of apparatus proposed for the same purpose by Birmingham* and Atkins† cannot

* U.S.A. Patent, 342,421, May 25, 1886.
† German Patent 45,774, November 27, 1887. [English Patent, 12,295, September 28, 1886.]

be considered as improvements. The latter, especially, even if it be possible to find a suitable material for some parts of the apparatus, would require most careful treatment, and frequent repairs during use, to retain it in serviceable condition.

Even the latest electric amalgamators show few special novelties. Edwards[*] places carbon anode-plates on the vertical side walls of a vessel, covers the bottom with a layer of mercury as cathode, and by means of a stirring apparatus holds the ore in suspension in an electrolyte consisting of an aqueous solution of potassium cyanide. Danckwardt[†] provides a barrel amalgamator with an equipment for electrolysis. The apparatus consists of a revolving iron cylinder, which is provided with a suitable lining (material not specified), and serves as anode. Guide plates are made to project into the interior from the walls of the cylinder for the purpose of throwing the ore, during the revolution, on to the cathode, which consists of an insulated and amalgamated copper plate cylinder placed within the iron barrel in the direction of its long axis. The copper cathode is removed from time to time, after suspending the rotation and electrolysis, in order to separate the amalgam from it. The solution is filtered from the suspended ore particles and is again used in another apparatus, either directly or after separating the dissolved gold.

Ludwig[‡] goes back to the launders to accomplish his electrolysis. In a wooden launder is a zinc plate provided with riffles which contain mercury. The zinc plate with the mercury forms the cathode. A cover is provided at the upper end to spread out the material as it enters, and to force it into contact with the zinc plate whilst diminishing the rate of flow of the particles of ore. Resting on this cover are copper (!) rods, which serve as anodes. The inventor anticipates that the cover, which consists of felt or flannel or the like, will take a part in the distribution of the electric current.

Haycraft's process, which, according to the *Engineering and Mining Journal*,[§] has been put to a practical test at Adelaide, consists in the electrolysis of a solution of salt in which gold ore is maintained in suspension. An iron electrolyte vessel with a heating arrangement is employed, and a layer of mercury on the bottom of the vessel serves as cathode. The ore is suspended in a solution of salt, and is kept in motion by mechanical stirrers, which are attached to a spindle, and are provided with carbon blocks as anodes. The larger particles of gold in the ore sink readily to the bottom and become amalgamated as in ordinary gold extraction processes, whilst the lighter and smaller particles

* U.S.A. Patent 518,543, April 17, 1894.
† U.S.A. Patent 526,099, September 4, 1894.
‡ U.S.A. Patent 527,150, October 9, 1894.
§ *Engineering and Mining Journal* (New York), 1895, vol. lix., p. 490.

of float-gold are dissolved by the chlorine liberated at the anode, and the resulting solution of chloride is electrolysed by the current, the metal being deposited upon and dissolved by the mercury cathode. The electrolysis is effected at a boiling temperature. After about an hour the ore-slimes are run out into a reservoir, from which they are led to a percussion-table for the purpose of recovering any detached particles of mercury or amalgam that may be caught in them. The tailings passing from here are conveyed to a reservoir in which the ore particles are deposited, whilst the clear solution is separated from them and again brought into use.

Gmehling's Experiments.—The testimony given by Gmehling[*] as to the working of electrical amalgamation processes is very unfavourable. He writes: " When I undertook the management of the works (Huanchaca, Bolivia), amalgamation was effected with the aid of an electric current generated by a Weston dynamo. The corrugated side plates and the copper bottom of the amalgamator were connected with a copper wire and made the positive electrode. In the uppermost portion of the pan, for about one-third of the distance down, a leaden ring was suspended to serve as the negative electrode. The current strength in the various pans ranged from 10 to 20 amperes.

" The practical utility of this so-called improvement appeared to me (Gmehling) very doubtful, especially as, in the course of my experience in the United States and in Mexico, I had never seen the electric current utilised in this way, although I had visited many and important amalgamation works. But in order to dispel any doubts upon this point, I made a number of experiments : (1) With a Weston machine, which gave a current of 10 to 40 amperes with some amalgamators in circuit; and (2) with a Gramme machine, which gave on an average a current of 45 amperes and 70 volts.

"After 55 experiments I was led to the conviction that an electric current of low potential does not assist amalgamation; the time required for the work was not appreciably lessened, and the percentage of precious metal in the tailings remained the same. On the other hand, there is no doubt that currents of high potential shorten the period of treatment; amalgamation, in 14 experiments, required about 40 minutes less time than usual, but the extraction of silver showed no improvement.

" These results led to the abandonment of the electrical method, since the considerable expenditure involved did not correspond to the small advantage that was gained. I worked from the 1st of October, 1889, without the aid of electricity, and obtained by accurate and suitable treatment a better result, both in regard to extraction of silver and loss of mercury, only the amalgama-

[*] A. Gmehling, *Metallurgische Beiträge aus Bolivia*, 1890.

tion required a somewhat longer time. The following table give
the results in a concise form :—"

METHOD.	Period of Experiment, 1889.	Silver left in Tailings.	Loss of mercury in oz. per mark of reduced silver.	Duration of Process.
		Per cent.		
Electric Amalgamation,	Jan. to Oct.	0·052	2·75	4 hr. 58 m.
Ordinary ,,	Oct. to Dec.	0·0356	2·39	5 hr. 10 m.

Electrolysis of Ores without the Aid of Mercury.—No one
will maintain that the unfavourable results hitherto obtained
are to be ascribed to the mercury, but a short account may be
given of the proposals to electrolyse ores without the aid of
mercury.   First to be considered are the apparatus of Cassel,[*]
and of the Cassel Gold Extracting Company,[†] which were
brought before the public in the years 1884 to 1887, and which
have become so well known through Exhibitions,[‡] and through
the journals, that, in view of their complete impracticability,
any detailed discussion of them is unnecessary.   A drum of
cylindrical or polygonal cross-section was made of some porous
material, and mounted so that it might be rotated about its long
axis, which was placed horizontally ; within the drum were a
number of carbon rods placed parallel to the walls, and about
half-immersed in a vessel containing a liquid in which a metal
plate cathode was suspended.   The gold of the ore was to be
chloridised within the cylinder and deposited on the cathodes
outside.   The electrolyte was a solution of common salt
rendered alkaline by lime.   It may be safely recognised that the
apparatus is not of practical utility if it be remembered that
it might have to be used in the treatment of ores containing
less than a hundredth or a thousandth part of one per cent. of
gold ; that, in order to obtain a pound weight of gold, from
5 to 50 tons of ore might have to be introduced into, rotated
within, and discharged from, the apparatus ; that the carbon
anodes, which even in clear solutions of salt are quickly
destroyed, would only last during the extraction of about 1 ton
of ore ; and, finally, that a company with a large capital was
formed and worked this process for the space of a year.

Body's process and apparatus [§] has already been described
in the Chapter on *Copper* (p. 223).   It testifies to a better

* U.S.A. Patents 300,950 and 300,951, June 24, 1884. [English Patent
3873, August 9, 1883.]
† U.S.A. Patent 362,022, April 22, 1887.   German Patent 38,744,
May 14, 1886. [English Patent 8574, July 15, 1885.]
‡ Inventions Exhibition, London, 1885.
§ U.S.A. Patent 333,815, Jan. 5, 1886.

appreciation of the difficulties to be overcome. Although the patent shows a distinct advance, it will be found better, in cases where ores have to be extracted with ferric solutions, to treat them with the liquid outside the electrolysing vessel.

The forms of apparatus patented by Stolp * have several good points, but even assuming that in all other respects, including the yield of metal, it were faultless, it could scarcely fulfil its object, owing to the rapid consumption of the anodes—large carbon cylinders and plates —which are too costly. It must not be forgotten that for every 1 lb. of gold recovered, some 100,000 lbs. of foreign material must be passed through the apparatus, and that this material is often very hard in character, and likely to cut through the soft anode plates very quickly. In one apparatus (Fig. 150) the anode consists of a vertical carbon cylinder, C, which may be rotated around its long axis, W. The cylinder is closed above and below, and beneath is connected with a conical projection, H. The upper part is closed by a cone, G, on which is placed a hopper, F. The ore, fed into the hopper with the solution of a metallic chloride, passes over the cone, and so over the surface of the rotating cylinder. D is a diaphragm, and E a cathode of sheet copper. Fig. 151 shows
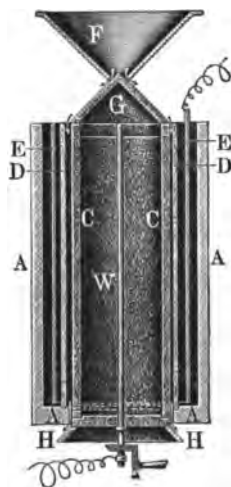
Fig. 150.
Stolp's gold-extraction apparatus.
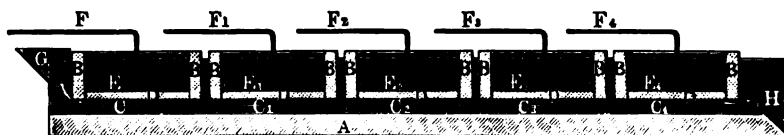
Fig. 151.—Stolp's modified apparatus.

another modification of the apparatus. On the bottom of a long vessel, A, slightly inclined towards the end, H, is laid any convenient number of carbon plates, C, C_1, C_2, &c. Above each of these plates is a vessel, B, which has the same length and width as the corresponding carbon plate. The bottoms of these vessels are formed by the diaphragms, D, above which the copper plates, E, E_1, E_2, &c., are suspended horizontally from the rods, F, F_1, F_2, &c. The whole apparatus is immersed in the solution of a metallic salt, but only to such a depth that the liquid cannot

* German Patent 41,061, Nov. 12, 1886.

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flow into the vessels, B, which contain pure sodium chloride solution in sufficient quantity at least to cover the plates, E. The ore is introduced through the hopper, F, and, the apparatus being gently shaken, it flows down the slanting floor towards H, whence the tailings flow away after extraction. In all modifications of the arrangement the chlorine liberated at the anode acts upon the ore particles which pass over their surfaces, and converts them into chlorides, so that no free chlorine escapes.

There remains yet to be mentioned the process introduced by Hannay. The first patent * protected the conjoint action of chlorine, electricity and a cyanide; in the second† the cyanide alone was used with the current; and in the third, ‡ a mercury cathode was employed in addition to the latter. The process received the high-sounding title of "The Universal Gold-Extracting Process," and met with ample support from the public.

Amid the large number of proposals for the electrolytic extraction of gold directly from the ore, the above are those which are most characteristic, or at least are those concerning which most has been said or written. But they are nowhere in operation.

Causes of Failure.—The causes of the failure of these processes hitherto have already been explained in part. The chief difficulty is that large masses of ore have to be kept in motion within the apparatus for a long time; and as they are suspended in water, or in the solution of a salt, they are accompanied by considerable quantities of liquid. Moreover, the solutions or the ores employed contain only a minute proportion of the metal to be extracted. It is sufficiently evident that, for the electrolysis of such mixtures, either the time required for the process will be very great, because the current density, and therefore the E.M.F also, must not exceed certain limits which depend upon the quantity of metal present. If this be not attended to, a considerable (possibly even the greater) part of the electrical energy applied will be expended in effecting subsidiary reactions, as soon as the low current density, which corresponds to the proportion of precious metal in the ore, has been exceeded. In the processes that have as yet been publicly described choice must be made between these two alternatives, and it may fairly be stated that neither is adapted to afford a solution of the problem. But many inventors act as though the electric current can have no action upon anything but the gold particles in the ore; and they almost appear to consider that it is endowed with life, attributing to it more intelligence than they themselves possess.

* English Patent 14,061, Nov. 2, 1886.
† English Patent 14,966, Sept. 22, 1890.
‡ English Patent 19,181, Nov. 25, 1890.

Very few inventors in this field appear to have any knowledge of the durability of the materials of which the electrodes are prepared, or of their behaviour in regard to the various electrolytes or the substances contained in them. It may suffice, by way of example, to refer to the Cassel apparatus in which the particles of ore are given the opportunity for the space of an hour to polish or grind so t carbon rods, in order to dissolve a proportion of gold so small that it might scarcely suffice to pay for the carbon consumed. S i again the demands upon the electrolytes, especially upon cyanides, are astonishing. All the chemical text-books insist sufficiently upon the readiness with which cyanides are decomposed, and in consequence of this instability the cyanide solutions are kept as far as possible from contact with the air when they are used for the simple extraction of gold ores. Nevertheless, the inventors of patent processes pass a current of air through cyanide solutions, or agitate the liquids in the presence of air, at any required temperature, and always with the desired result—at least, in the patent specifications. The deposited gold also is able, according to the patent specifications, entirely to alter its usual characteristics. Thus it may have to bear the roughest mechanical treatment, and yet it must adhere firmly to the desired metallic surface; and it is called upon to withstand the grinding action of the fine and hard particles of ore suspended in water. It is only necessary to bring a metal bar well coated with a substantial film of gold into any of the usual forms of apparatus for treating gold ores (whether as cathode or not), and the question whether the gold remains in place will soon be answered in the negative.

Jory's Process.—After all the negative results above described, the process of Jory* may be referred to, in which the ore is mixed with the electrolyte. It possesses, at least, two distinct advantages as compared with those already mentioned—neither carbon anodes nor diaphragms are used. It remains yet to be seen whether it will be successful. The apparatus consists of launders, in which amalgamated copper plates are hung parallel to the direction of the stream carrying the ore, and at very short distances apart. The ore, in an exceedingly finely divided state, is carried in suspension in water through the launders, whilst an alternating current is passed between the metal plates. During the process the space which the pulp has to traverse between the plates is about $\frac{1}{80}$ in. The chief requisite for this process is that the ore shall be crushed as fine as possible, and that it shall be passed through the launders in the form of a fine mud. No further information is at hand concerning the practical working of the process.

Solution of the Gold by Chemical Methods, followed by

* *Engineering and Mining Journal* (New York), 1894, vol. lviii., p. 440.

**Electrolytic Precipitation of the Metal from the Liquid —
Early Suggestions.**—It was pointed out in the first edition of
this book that when a metal like gold, which is easily separated
from its solutions, even without the aid of the electric current,
is to be deposited electrically, it would be advisable to effect the
solution of the metal outside the anode chamber of the electro-
lyte vessel. The author cannot lay claim to having suggested
the only method which apparently can be practically used at
present for the treatment of gold-bearing materials, for the firm
of Siemens & Halske had already proposed a similar treatment
for sulphide ores and products of copper, but it is satisfactory to
him to find that the results obtained in practice have completely
justified his prediction.

Siemens-Halske Process.—It was again Siemens & Halske
who were the first to obtain practical results in this field; and
the following details of their process have been taken from private
communications from the directors of the firm. The principles
upon which the process is based are as follows :—Gold-bearing
ores or amalgamator tailings are leached with dilute solutions of
potassium cyanide; gold thus passes, for the most part, into
solution as already explained ; the resulting liquid is electrolysed
with iron anodes and lead cathodes, and when the latter have
received a sufficient deposit of gold they are removed from the
bath, dried, melted, and cupelled for the separation of the gold
from its alloy with lead.

For the Siemens process, only those ores or tailings may be
employed which contain no appreciable quantity of substances
that would cause a loss of cyanide, among such prejudicial con-
stituents being free sulphuric acid, ferrous and ferric sulphate,
and all base metals and metallic compounds that are soluble in
cyanide solution. If such constituents be soluble in water
they may be washed out of the ore prior to treatment with
cyanide; or lime may be used to neutralise their effect. Again,
the solvent action of the potassium cyanide upon the gold is
slow and incomplete when the precious metal is present in the
form of *large grains*. And, finally, the percentage yield or
efficiency of the process is less when the *proportion of gold* in
the raw material is *very high*. From the above it will be readily
understood that the most suitable materials for this treatment
are quartzose or undecomposed pyritous ores or tailings, which
contain a medium or a small proportion of gold, in metallic form
and in a state of fine sub-division.

*The preparation of the auriferous material for the leaching
process* consists solely in pulverising it as fine as possible.
Tailings, however, may be treated directly. When the cyanide
works are not attached to an amalgamating plant, a **crushing
apparatus** is the prime essential, and with this must be pro-
vided the **leaching and electrolytic plants, cupelling**

furnaces, and reduction furnaces for treating the litharge obtained in cupellation, as well as the various requirements for melting, casting, and the like. Suitable forms of stamping and crushing machinery are described in all the larger works on metallurgy.

The extraction or leaching vats are large iron vessels, holding about 3500 cb. ft. The auriferous sand or tailings are charged into these, the cyanide solution is poured over the mass, and the whole is stirred mechanically. In some cases the stirring is not only superfluous, but even disadvantageous, *because all unnecessary contact of the solution with air is especially to be avoided*. In working ores or residues containing but little gold, the pulverulent material usually contains sufficient oxygen for the reaction given in Elsner's equation :—

$$Au_2 + 4KCy + O + H_2O = 2KCy . AuCy + 2KOH.$$
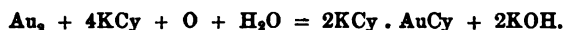
and each further addition of oxygen, which cannot but be favoured by stirring, must lead to oxidation, and, therefore, to loss of cyanide. It will be self-evident that the stirring mechanism will be differently constructed for sandy and clayey materials; and chemical technology is so well provided with suitable means for dealing with the one or the other class, that there is no necessity to enter into any further particulars in this direction. After the leaching is complete the solution is transferred to the precipitation plant, and will usually contain about 8 parts per million, or 12 grains per gallon, of gold.

The **precipitation plant** at the works of the Rand Central Reduction Company, at Worcester, in the Transvaal, consist of four iron vats, each measuring 20 ft. × 8 ft. × 4 ft. Within this are suspended sheet iron anode plates, each 7 ft. long by 3 ft. wide and ⅛ in. thick; and lead plates of the same size are supported on light wooden frames as cathodes. The principal conductors are laid lengthwise along the rims of the vats, and connection is made with them in the usual way. To promote the circulation of the liquid in the vats, the electrodes are so arranged (by resting some on the bottom and suspending others) that a space is left alternately above and below them, through which the solution may pass. The electrodes are kept at a distance of about 1⅛ in. apart by strips of wood attached to the bottom and sides of the vats. The current density is about 60 amperes per sq. metre [5·6 amp. per sq. ft.] at an E.M.F. of 4 volts.

The cathode material must answer to the following requirements :—(1) The deposited gold must remain adherent to it; (2) in order to reduce the cost of the plant it must be used in thin layers, sheets, or plates; (3) it must be easily separated from gold subsequently; and (4) it must not be more electro-

positive than the anode material. As mercury would be too costly, especially having regard to the low current density, lead. has been selected as the most suitable substance. Carbon is not sufficiently durable for anodes, and iron is therefore used; it is to some extent attacked, but it forms Prussian blue, which can be worked up again into potassium cyanide.

The electrolyte tanks are kept locked up, and at intervals of a month the leaden cathodes are removed, one at a time, without interrupting the current, and replaced by fresh plates. The old cathodes will have been coated with from 2 to 12 per cent. of gold, which is separated by cupellation. The consumption of lead amounts to about 750 lbs. *per mensem*, corresponding to a cost of about 1½d. per ton of ore. After the precipitation of the gold, the solution is returned to the leaching vats, after adding sufficient potassium cyanide to make good the loss during extraction and precipitation.

Estimated Cost of Siemens-Halske Process.—The results of working are as follows:—*Potassium cyanide* is decomposed not only in the process of dissolving the gold and other metals, but also by the action of carbonic acid in the air. The proportion consumed varies in different cases, and depends upon the composition of the ore or tailings. In one instance in which 3000 tons of tailings, containing 5 dwts. of gold per ton were treated *per mensem*, the consumption of cyanide amounted to ¼ lb. per ton of tailings.

The labour and power required may be reckoned as follows:— For an installation capable of treating 3000 tons of ore a month there would be required five labourers (native) and two supervisors. This plant calls for an expenditure of about 5 H.P. for the electro-deposition of the gold, and about 25 H.P. for the whole work, including electric lighting and electrical power transmitted for the stirring mechanism.

The cost of the installation, in respect of the vats, and the necessary apparatus for extraction and precipitation, must obviously be very different in different places; it may, however, be estimated according to the quantity of ore or tailings to be treated. It may be assumed that each extraction vat works with its full charge of tailings, and is charged and emptied once every day; and that from three to six such vessels are employed according to the character of the ore and the number of leachings required. The application of the dynamos and the electrical portion of the installation may, of course, be restricted to the actual deposition of the gold; but it will be found advantageous to generate at the same time current sufficient for the electric lighting of the whole establishment, and for the electrical transmission of power to the pumps and stirring machinery. For a plant capable of treating 3000 tons of tailings *per mensem*, the capital outlay on the electrical installation, exclusive of freight,

duty, or erection charges, may be taken at £250 for the electrical installation in connection with the precipitation, and £750 for that required for lighting and transmission of power.

The working charges of the plant above described in the Transvaal, treating 3000 tons of tailings a month, were as follows * :—

	Per mensem.	Per ton of tailings.
Charging and emptying of vats (by a contractor and his labourers), . . .	£125	10·0d.
Potassium cyanide, ...	75	6·0
Lime, ...	15	1·2
Soda, ...	6	0·5
Sheet lead, ...	14	1·1
Iron plate, ...	28	2·2
White labour, ...	65	5 2
Native labourers (wages and food), . .	20	1·9
Fuel, ...	57	4·6
Store and general charges, ...	41	3·2
Approximate total, ...	£450	3s.

The extraction efficiency amounted on the average to 70 per cent. The profits of the process may be reckoned thus :—The assay value of the tailings averages about 5 dwts. per ton, and since 70 per cent. of this is recovered, about 520 ozs. of gold should be recovered.

* [Since the publication of the above statement of costs at the Worcester Works, a revised account has been published by von Gernet in a paper read before the Johannesburg Chemical and Metallurgical Society, in October, 1896. These figures are appended as an example of the latest practical results in South Africa, with a plant capable of treating 500 tons of tailings per diem.

	s.	d.
Filling, ...	0	10·0
Potassium cyanide, . . .	0	3·4
Lime, ...	0	0·5
Lead, ...	0	1·5
Iron, ...	0	0·3
White labour, ...	0	5·0
Native labour, ...	0	1·9
Fuel and power, . . .	0	4·0
Store and general charges, . .	0	3·2
Charge extra cost of plant, . .	0	0·5
	2	6·3

This reduction does not appear at first to be very great, but when calculated upon the monthly outturn, it will be found to be really very large.—TRANSLATOR].

520 ozs. of unrefined gold,	.	.	.	.	£1,850
Deducting working charges, &c.,	.	.	.		700
Profit *per mensem*,			.	.	£1,150

But from this must be deducted the value of the tailings and the manager's salary, leaving, however, an ample margin for interest, amortisation, and dividend. The above-named Rand Central Ore Reduction Co. has, in the first year of work at the Worcester installation, paid a dividend of 25 per cent., even after writing off a considerable sum.

Comparison of Electrolytic and Chemical Precipitation Processes.—The advantage of the electrolytic method of precipitation as compared with the chemical is very considerable. The latter method necessitates the use of comparatively strong cyanide solutions, because it is only from such liquids that the gold can be precipitated with any degree of completeness by metals like zinc. The electrolytic process is, however, capable of being used with more dilute solutions. The consumption of cyanide also is considerably reduced, as may be gathered from the following comparison. In the MacArthur-Forrest process solutions containing 0·3 per cent. of KCy are used, whilst in the Siemens process the strongest liquor contains 0·05 to 0·08 per cent., and others with only 0·01 per cent. KCy are also employed. A plant treating 3000 tons per month of tailings by the former process consumes cyanide to the value of £220 *per mensem*, whilst a similar plant worked by the Siemens system requires an expenditure of only £75 in the same time for the same quantity of raw material. It is true that the use of weaker solutions for extracting necessitates a longer period for solution, and, therefore, a larger installation of leaching vats; but this is of less importance than the high consumption of cyanide. A further advantage of the Siemens process is that the gold is obtained in the form of a solid deposit upon the leaden plates, whilst by chemical precipitation the gold is recovered as a loose powder mixed with particles of zinc. Further, by the precipitation of the gold on lead the troublesome purification and separation of the powdered gold in the zinc boxes is dispensed with; and at the same time the cupellation process for the separation of lead from gold is conducted without difficulty and enables the lead to be recovered, whilst the separation of the zinc from the gold in the older process by solution in acid or in other chemical reagents necessitates the loss of both zinc and acid.

The economy of the electrolytic, as compared with the MacArthur-Forrest, process is clearly shown by the fact that the cost of treatment per ton of tailings, in a work capable of dealing with 100 tons *per diem*, by the former process is only 3s., while

by the latter it ranges, according to Eissler,* from 7s. to 8s. It is thus clear why the successful method initiated by Siemens & Halske has recently been employed in preference to those of other inventors.

Later Processes.—Eltonhead † expects to obtain better results by electrolysing the cyanide solution of the gold with lead anodes and mercury cathodes; but practical metallurgists will not support this view.

Keith ‡ proposes to use a solution of mercury potassium cyanide for leaching, with the object of obtaining a greater extraction efficiency in regard to gold; and he therefore adds from 6½ to 13 lbs. of a soluble mercury salt to each ton of the cyanide solution containing from 0·1 to 0·5 per cent. of KCy. In the depositing vats the cathodes are amalgamated copper plates, 2 ft. square, arranged in the same manner as the electrodes in the Siemens vats; so that the solutions can only pass in zig-zag fashion, flowing past the cathodes in an upward and downward direction alternately. Between each pair of cathode plates, which are separated from one another by a distance of 2 ins., are placed from 8 to 10 porous vessels, 1 in. in diameter and 2 ft. in height, containing zinc rods as anodes. It remains to be proved whether in practice the greater expenditure on the electrolyte, the anodes, and the diaphragms, which are notoriously wanting in durability, will be compensated for by a higher yield of gold.

Pélatan and Clerici describe in an American patent specification § a complete scheme for a gold-extraction process, in which a cyanide leaching plant is combined with an electrolytic separating apparatus. The zinc anodes of the depositing vats act also as stirrers, and for this purpose a spindle is protected with a coating of zinc and provided with zinc agitators. Amalgamated copper plates laid upon the bottom of the electrolyte vats serve as cathodes. [In the English patent specification the anodes are described as horizontal iron shafts, with iron cylinders and wooden agitators.] A greater change in the method of work has been proposed by Gaze,‖ who uses the chloride of bromine as a solvent in place of the cyanide. The chloride of bromine is formed by electrolysing a mixture of sodium chloride and sodium bromide in vessels 3 ft. high and 2 ft. wide, containing porous vessels filled with water, which are used as cathode cells. In the outer vessels a solution of chloride of bromine is formed, and in the inner cells a solution of caustic

* M. Eissler, *The Cyanide Process*, London, 1895.
† *Elektrotechnischer Anzeiger*, 1895, p. 125.
‡ *Electrician*, 1895, vol. xxxiv., No. 637.
§ U.S.A. Patent 528,023, Oct. 23, 1894. [English Patents 2493, Feb. 5, and 11,478, June 12, 1895.]
‖ *Engineering and Mining Journal* (New York), 1895, vol. lix., p. 442.

soda. The former is brought into contact with the gold-bearing material in vessels which may be tightly closed; air is then pumped into them up to a pressure of from 3 to 4 atmospheres, and the mixture is allowed to remain at rest for from one to two hours under these conditions. The solution is then drawn off, and utilised for the treatment of fresh quantities of ore or tailings, until its solvent power for gold is neutralised, after which the dissolved gold is separated from it electrolytically.

If the last four proposals should prove to have such advantages over the Siemens process, that they are introduced into actual practice, they will at least prove that the method of work suggested by the author in the first edition of this book has received common recognition. The process of Siemens & Halske has shown that it is capable of affording practical results.

Uses of Gold.—Pure gold is employed directly in the production of chemical preparations of gold, for the gilding of other objects, and for the production of alloys with copper, silver, and other metals. The alloys of gold and copper containing up to 90 per cent. of the precious metal are used mainly for coinage* purposes, but in addition to this they are very largely employed for all kinds of jewellery and goldsmith's work, both in the massive condition and as a coating for other metals.

CHAPTER IV.

ZINC AND CADMIUM.

ZINC.

Properties of the Metal.—Zinc (Zn; atomic weight = 65; specific gravity = 6·9 to 7·2) is a bluish-white, lustrous metal, with a crystalline (hexagonal) structure. At ordinary temperatures it is brittle, but between 100° and 150° C. it becomes malleable, and may be rolled, hammered, or drawn into sheet or wire. At a higher temperature—about 200° C.—it again becomes so brittle that it may be crushed to a powder. It melts at 415°, and boils between 930° and 950° C. Its electrical conductivity at ordinary temperatures is about 0·27 that of silver. It has the power of dissolving or of being dissolved by most other metals; and with many it alloys in all proportions.

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* [The British standard gold for currency is a 22-carat alloy; that is to say, it contains 22 parts in every 24 (or 91·6 per cent.) of gold. The residual alloying metal for coinage is copper, for jewellery it may be copper or silver separately or together.—TRANSLATOR.]

Lead, however, dissolves only a little zinc (less than 1·5 per cent.), and zinc but little lead (less than 2·5 per cent.).

Metallic zinc has a comparatively high power of resistance to the action of oxygen and other constituents of the air. It is true that in moist air it rapidly becomes covered with a greyish film of basic carbonate; but this coating is very dense, and clings firmly to the surface of the metal, which is, therefore, practically protected by it from further oxidation. Above its boiling point, however, zinc burns readily either in air or in carbonic acid. Water has but little action upon the metal at ordinary temperatures, although at a red heat it forms zinc oxide and hydrogen (see *Lead Refining*). Zinc burns in chlorine to zinc chloride, but does not easily unite directly with sulphur; a phosphor-zinc may, however, be readily formed by introducing pieces of phosphorus into the melted metal.

On account of its strongly electro-positive character, and the great solubility of most of its salts, zinc is easily dissolved by dilute acids; but the solution takes place the more slowly, the purer the metal used. Nitric acid is in part converted into ammonia by its action upon zinc. The electro-chemical characteristics of the metal are shown by the fact that it is capable of separating most of the heavy metals from their salts, and that it is soluble in solutions of the alkaline hydroxides with evolution of hydrogen. The high electrolytic pressure of solution of zinc makes it a good anode material for galvanic batteries.

With acids, zinc forms only one series of salts, which are derived from the oxide, ZnO; with the alkalies, zinc oxide (or hydroxide) plays the part of an acid, and forms salts which may be regarded as derived from the hydroxide, $Zn(OH)_2$, the latter being considered as a dibasic acid.

Occurrence of Zinc in Nature.—The more important of the natural compounds of zinc are the sulphide, zinc blende, ZnS; the carbonate, calamine, $ZnCO_3$; some silicates, electric calamine, $Zn_2SiO_4 + 2H_2O$; and complex zinc ores, such as franklinite, consisting of silicates and carbonates usually containing less than 20 per cent. of zinc.

Extraction of Zinc.—In the extraction of the metal, not only the above ores have to be treated, but the so-called grey oxide, and furnace incrustations from iron-smelting blast-furnaces and other metallurgical furnaces are also employed; and latterly the residues from the roasting of zinc-bearing pyrites have also been used. Apart from the methods by which zinc compounds, such as zinc white or zinc sulphate, are obtained from the ores, there are only two metallurgical processes practically in use the roasting and reduction process, and electrolysis.

The Roasting and Reduction Process.—This process may be used for the treatment of most zinc ores. Some ores that contain but a small proportion of zinc require a preliminary

wet process of mechanical concentration; but they (especially zinciferous blendes or spathic iron ores containing zinc) often yield in this way large quantities of bye-products which cannot be used either in the lead or the iron smelting processes. Zinc-bearing iron ores, and intermediate products from the dressing processes, containing insufficient zinc to be directly workable, have for some time been subjected to a roasting process followed by magnetic concentration. Roasting has the effect of converting both ferrous and ferric oxides into the magnetic oxide of iron; and this latter compound is then the only magnetisable substance present, unless, of course, metallic iron itself should by any possibility be there. It is self-evident that if the iron be initially present in the ore in the form of magnetite or of magnetic pyrites, the roasting process would not be required. If roasting be necessary, blast furnaces, reverberatories, or revolving calciners may be employed. The raw or roasted ore, as the case may be, is then classified into particles of uniform sizes, and submitted to magnetic separation, by which the iron-bearing particles are extracted from those of zinc- or lead-minerals and gangue stuff. Electro-magnetic separators are interesting from the electro-metallurgical point of view; but there have been over 170 patents for such separators granted in the United States alone, and it would therefore be impossible to enter fully into the subject here.

The ore, after having been sufficiently concentrated by one process or another, is roasted. Carbonates may be calcined in simple kilns, such as are employed in lime burning or for the calcination of spathic iron ores. Blende is treated in specially constructed stage furnaces, of which the best forms known are those of Liebig and of the *Aktiengesellschaft Rhenania.*[*]

The roasted ores are so mixed together, and with the carbon necessary for reduction, that sufficient of the latter element may be present to prevent the formation of carbonic acid, and that the residual substance left after the reduction process may be as difficultly fusible as possible. To fulfil the latter conditions, it may often be sufficient to provide an excess of coal, the coke from which absorbs any fused products of the reaction. If much silicate of zinc or leady impurities be present in the ores, an addition of magnesite, dolomite, or bauxite is recommended, in order that the silicates left in the residue may be rendered more refractory. The process of reduction is conducted almost exclusively in retorts, the zinc being converted into a vapour which is afterwards condensed. According to the **Belgian** system, a number of small tube-shaped retorts are arranged in parallel rows, one above another, in a shaft furnace. In the **Silesian** process a smaller number of retorts is used, but these are larger than those employed in the Belgian furnace, and are

* G. Lunge, *Soda industrie*, 2nd ed., vol. i. (sulphuric acid), 1893.

laid side by side, usually in only one row. A combination of the two systems is in use in Rhenish-Westphalia; not more than three rows of medium sized retorts being placed one above another. The furnaces are almost always heated by gaseous fuel, the air used for combustion being pre-heated, either by the regenerative (Siemens) or the recuperative system.

The condensation of the zinc vapour is generally effected in clay condensing tubes connected immediately with the fronts of the retorts, and in sheet-iron cylinders, which are attached to the clay tubes at the beginning of the distillation. The zinc is deposited in the condensers, partly in a pulverulent form as "zinc-dust," and partly in the liquid state. The details of the arrangements of the furnace and of the method of conducting the operation are to be found in metallurgical text-books.

ELECTROLYSIS.

There can be no doubt that the purely metallurgical methods of extracting zinc must be classed among the most unsatisfactory and wasteful of smelting processes; and the electrolytic separation of the zinc, therefore, must always be an attractive and legitimate problem. In spite, however, of all endeavours, the extraction of zinc by electrolysis has not yet advanced beyond the experimental stage, although operations on a larger scale have recently been commenced in the "Electrolytic Zinc Works at Duisburg." The mere reduction of the zinc by electrolysis is by no means a difficult task; but the problem of obtaining the metal with a sufficiently low consumption of power in the form of sound plates suitable for direct use in zinc rolling is, apparently, less easy to solve.

As in the case of the metals hitherto described, the experiments in zinc extraction have been conducted on three separate lines. In the oldest methods proposed, zinc solutions were to be ·electrolysed with anodes composed of the ore itself. The first process that gave any practical result on a large scale was that in which a zinc alloy (the zinc-silver alloy of the Roessler-Edelmann process) was used as anode; but the final solution of the problem will probably be found in the electrolysis of dissolved or fused zinc salts with the aid of insoluble anodes.

1. **Electrolysis of Solutions of Zinc Salts with Anodes of Zinc Ore.**—Luckow, who, in a German patent specification,* was the first to propose the technical application of electrolytic processes to zinc extraction, appears to have regarded the deposition of the metal in a cohesive state as impracticable at the time of his patent, for he writes :—

"By the electrolysis of concentrated solutions of zinc salts a

* German Patent 14,256.

granular zinc is obtained, whilst the liberated acid is allowed to act upon zinc ores, polarisation being prevented by chemical or mechanical means. A long trough is used as the electrolysis tank, in which the electrodes are placed alternately one behind the other in positions parallel to the short side of the trough. The cathodes are zinc plates, and beneath them are placed diaphragms of cloth stretched upon frames to receive the metal which separates from the cathode plates. Between the zinc plates are cells with open lattice-work sides (or of basket-work) projecting somewhat above the solution in the vat, and filled with a mixture of carbon and zinc ores, or roasted or metallurgical products, or with carbon alone. A bar of metal is inserted into this mixture from above in order to make metallic contact with the conducting mains.

"When solutions of zinc chloride are thus electrolysed with a carbon anode, the chlorine liberated at this pole is removed either mechanically by a current of air, or chemically by the introduction of sulphurous acid. If, however, the anode consist of a mixture of coke and blende, the free chlorine attacks the latter and effects the solution of the zinc. A slightly acidulated solution of common salt may be used as electrolyte in this case instead of zinc chlorides."

Blas and Miest* proposed to crush the blende until it would pass through a sieve of 5 meshes to the linear inch, and then to unite the particles into plates under a pressure of 100 atmospheres; the plates were then to be heated and again compressed, in order to obtain anodes suitable for their electrolytic process. They considered that their process offered great advantages as compared with those in common metallurgical use, and with other methods which had been proposed up to that time. But it has, nevertheless, made no headway.

It is unnecessary in this place to enter into a detailed account of the difficulties resulting from this method of work, after what has been written in the chapter on copper concerning the use of sulphide ores as anodes. The use of sulphurous acid proposed by Luckow as a depolarising agent in connection with insoluble anodes will be referred to again later.

2. **Electrolysis of Solutions of Zinc Salts, Using Anodes of Crude Zinc or Other Zinc Alloys.**—Simple as this method of extraction appears from the theoretical standpoint, it is wrecked even at the outset, in part by the numerous difficulties arising from the composition of the raw material, but mainly by those connected with the electrolysis of aqueous solutions of zinc salts. The refining of crude zinc is at present too expensive, for the electrolytic treatment of zinc with the intention of producing a metal that may be rolled necessitates the use of very

* Blas and Miest, *Essai d'application d'électrolyse à la métallurgie*, Paris, 1882.

great care, and therefore demands skilled labour, whilst it
requires a high expenditure of power as compared with other
metals. The zinc crusts produced in desilverising lead by the
Rössler-Edelmann process have, however, shown themselves to
be suitable to electrolytic separation.

Treatment of Zinc Crusts from the Desilverisation of Lead.—
The zinc crusts from the original (Parkes) process on the
contrary have not been found available as an anode material.
These crusts, which consist of a mixture of lead-zinc, zinc-silver,
and other alloys, may contain as much as 77 per cent. of lead,
12 per cent. of zinc, and 2·4 per cent. of silver, in addition to
other metals and oxides. Experiments have been made for a
long period at the *Königliche Friedenshütte*, at Tarnowitz, in the
electrolytic separation and deposition of the zinc contained in
the crusts, the silver-bearing lead being left as an insoluble
substance at the anode. Rösing[*] has described these experiments
as follows :—

"This electrolytic treatment of zinc crusts differs from other
electro-metallurgical processes, as, for example, the refining of
copper, the Keith process of separating silver from work-lead,
and the Hermann process of purifying commercial zinc, in that
in these latter instances the metal to be dissolved and deposited
electrically forms by far the largest constituent of the material
under treatment, whilst in the case of zinc it often does not
exceed the one-tenth part of the whole mass. The result of this
is that as soon as the zinc is dissolved, which initially was in
immediate contact with the electrolyte, a surface is formed con-
sisting of lead and silver, which are the insoluble materials of
the anode. At this juncture the current may be stopped, since
otherwise, according to the E.M.F. employed, either a separation
of hydrogen will occur, or else the current will of itself cease to
to pass (?) if insoluble anodes be used.

"It is evident that the extraction of the zinc will always be
highest when the largest surface is exposed to the solution. For
this reason the alloy is used in the pulverulent condition, since,
on account of its brittleness, it cannot satisfactorily be used in
the form of thin plates. The electrodes must, therefore, form a
horizontal layer. Circular wooden vats are employed, in which
the zinc crusts rest upon a leaden plate, and so form the anode.
The cathode is a zinc plate resting on insulating supports above
the anode. In order to maintain a circulation of the electrolyte
several vats are so placed at different levels that the liquid,
which runs into the uppermost vats from a reservoir above.
overflows into the one next below it, and then in turn through
each of the others until at last it flows from the last of the series
into a second reservoir, and may be used over again. After
the current has passed through the solution for some time, the

[*] *Dingler's Polytechnisches Journ.*, 1887, vol. cclxiii., p. 93.

anode mass will consist of kernels of unaltered alloy, surrounded by a layer of metal from which the zinc has been extracted; the kernels are separated by a process of liquation, and are then treated again. Thus, in turn, zinc is removed by electrolysis and lead by liquation. The small quantity of lead and silver contained in the deposited zinc is not lost, because the metal is used to desilverise a fresh portion of lead, whilst the silver in the rich lead obtained by liquation is recovered by cupellation; and the litharge produced in the last-named process is again reduced to metallic lead."

It is evident from the above description that the frequent interruptions of the process for the liquation of the lead from the kernels must be exceedingly troublesome. In the account[*] published in commemoration of the hundredth anniversary of the *Königliche Friedenshütte*, it is stated that this process had never passed beyond the experimental stage, partly for the reasons assigned above, and partly because there would not be a sufficient return for the high cost of the installation as compared with that required for the distillation process.

Much more favourable results were obtained in treating the crusts from the Rössler-Edelmann process of desilverising work-lead. This process, as is well known, consists in using zinc containing a small (about 0·5 per cent.) proportion of aluminium in place of pure zinc. This small quantity of aluminium is used to ensure that the zinc may be free from oxide, but it has the very beneficial effect of leading to the production of zinc crusts, containing far more silver and less lead than those hitherto obtained. The liquated crusts contain from 20 to 40 per cent. of silver, with zinc ranging up to 70 per cent., and a small proportion of lead and copper. It is evident that such a material must give better results as an anode alloy than one that may contain nearly 80 per cent. of lead. Only meagre accounts have so far been published concerning the conditions of electrolysis in this case; but these conditions have only been ascertained with much trouble and expense, and it is unreasonable to expect that they shall be given freely to the public.

The electrolyte consists of a solution of the chlorides of zinc and magnesium of specific gravity 1·2 to 1·27, and is purified from time to time by the addition of a basic zinc salt $ZnCl_2 . 3ZnO$. The cathodes consist of vertical discs mounted on a horizontal shaft, so that they may be rotated, the shaft being mounted above the top level of the liquid. No information has been published concerning the current density and the temperature of the bath.

The zinc obtained is very pure, and contains usually 99·92 to 99·94 per cent. of zinc, with at most 0·05 per cent. of lead, 0·02 per cent. of copper, and 0·0044 to 0·0099 per cent. of

* Printed by Ernst and Korn, Berlin.

iron; it may also contain up to 0·002 per cent. of silver. On account of its purity, it commands a better price than ordinary commercial zinc. The insoluble constituents left at the anode remain in the form of a mud, which on drying is found to contain about 75 per cent. of silver, 12 per cent. of lead, and small proportions of insoluble chloride and oxide of silver, copper zinc, iron, and lead. The oxides of copper, zinc, and iron are removed by treatment with dilute sulphuric acid, and any silver chloride that may be present is reduced by means of iron filings or turnings. The residue, after drying, should then contain from 80 to 85 per cent. of silver and about 15 per cent. of lead; it requires only to be refined by oxidation.

Electrolytic Refining of Zinc.—No further accounts have been published concerning the treatment of zinc alloys or the refining of impure zinc on a large scale. Several patents have been taken out for zinc refining by electrolysis, but they contribute little that is worthy of remark. Thus, for example, Hermann * recommends the use of solutions of the sulphates of zinc, or alkali metals, or of zinc and alkaline-earth metals, with crude zinc plates as anodes, whilst Watt † employs a vegetable acid as electrolyte with crude zinc anodes. Some very useful hints may, however, be obtained in connection with the extraction of zinc, with or without zinc anodes, from publications which have been made independent of the patent office.

Kiliani's Experiments.—Mention must first be made of the work of Kiliani,‡ who determined the current densities that should be employed for the electrolysis of solutions of zinc sulphate of various degrees of concentration. When soluble anodes were used, and both electrodes consisted of zinc plates, he found that the evolution of gas was greatest when the current density was small, that it grew less as the current density was increased, and ceased altogether when 3 mg. of zinc were deposited per minute on each sq. cm. of electrode surface [= 0·3 grain per sq. in.]. This is shown in the table on the next page, to which the current density in amperes per sq. metre and square inch has been added, in order to facilitate comparison with the current conditions which have been found practically useful under other circumstances.

The deposits obtained with high current densities were, it is true, very solid, but they were formed to a large extent around the edges of the plates. With a 10 per cent. solution the best deposit was obtained by the use of a current density equivalent to 0·4 to 0·2 mg. of zinc. From very dilute solutions the metal was always precipitated in the spongy condition, and was accompanied by a considerable separation of hydrogen. Moreover,

* German Patents 24,682 of 1883, and 33,107 of 1885.
† English Patent 6294, April 29, 1887.
‡ *Berg- und Hüttenmännische Zeitung*, 1883, p. 251.

with a low current density zinc oxide was always deposited, as, for example, when a 1 per cent. solution was electrolysed with a current which threw down 0·0755 mg. of zinc per sq. cm. of cathode per minute (and with an E.M.F. of 17 volts). The available area of the electrode surface must, therefore, be adjusted to correspond with the strength of the current and the concentration of the solution. The solution with which the results incorporated in the following table were obtained was highly concentrated, having a specific gravity of 1·38.

Current density in		Amperes.		Evolution of gas in cubic centimetres per 1·5 grm. of zinc deposited.	Character of the Deposit.
Mg. of zinc per sq. cm. per minute.	Grains of zinc per sq. in. per minute.	Per sq. metre.	Per sq. in.		
0·0145	0·0014	7	0·005	2·40	Very spongy.
0·0361	0·0036	18	0·011	2·27	
0·0755	0·0075	38	0 021	0·56	
0·3196	0·0316	158	0·1	0·43	Denser, but still spongy at the edges.
0·6392	0·0632	316	0·2	0·33	Still easily rubbed off.
3·7274	0·371	1843	1·2	...	Very firm and a lustrous white ; with warty growths at edges.
38·7750	3·860	19,181	12·4	...	

The Experiments of Mylius and Fromm.—Mylius and Fromm[*] have recently determined the conditions under which absolutely pure zinc may be deposited. They point out that they do not consider the method of procedure used by them to be adapted for technical purposes ; but their account records so many facts that afford explanation of the condition obtaining in practice that a summary of some of the points will be useful, especially in connection with the refining of zinc. Concerning the action at the cathode, and with special reference to the formation of spongy zinc, and to the work of Kiliani, these authors express themselves as follows :—

"The cause of spongy zinc deposits has not yet been determined. Nahnsen[†] considers that they must be attributed to the oxides which are formed by the decomposition of the water, whilst others[‡] believe in the existence of a hypothetical hydride of zinc, ZnH_2, which produces a molecular alteration of the zinc. As we (Mylius and Fromm) are at present engaged in a special investigation[§] of porous metallic deposits, we are pre-

* Zeitschrift für anorganische Chemie, 1895, vol. ix., p. 144.
† Berg- und Hüttenmännische Zeitung, 1891, p. 393.
‡ Siemens and Halske (German Patent 66,592).
§ Cf. Mylius and Fromm, Berichte d. deutschen. Chem. Gesellschaft, vol. xxvii., p. 630.

vented from entering further at this time into the question of the mechanical formation of zinc sponge; we may, however, point out that its formation is accompanied by an absorption of oxygen, and that it always contains oxygen or basic salt. This is proved without doubt by the following observations:—

"(1) The spongy zinc will not dissolve in mercury without leaving behind a slight residue of oxide or basic salt, amounting usually to considerably less than 1 per cent.

"(2) The production of the sponge is induced by oxidising agents. Thus a 10 per cent. solution of zinc sulphate, which contains 0·01 per cent. of hydrogen peroxide, shows a formation of sponge even after two minutes with a current density of 1 ampere per sq. dm. [0·0645 amp. per sq. in.]. Or again, if the solution contain 0·1 per cent. of zinc nitrate in place of the hydrogen peroxide, a greyish-black deposit of zinc, containing oxide, will be formed after about one minute.* Or if a sheet-zinc cathode be spotted with oil of turpentine containing oxygen, greyish-black flakes, which are the first signs of sponginess, are formed at these places. The zinc sulphate solution employed in these experiments, when used for an hour alone and without oxidising agents, gave a smooth white deposit throughout.

"(3) The spongy zinc is produced only when the conditions are favourable to the formation of zinc oxide. A 10 per cent. solution of zinc sulphate, which was intentionally made somewhat turbid by precipitated oxide, gave a grey spongy zinc upon a sheet-zinc cathode after five minutes of electrolysis with a current of 1 ampere per sq. dm. [0·0645 amp. per sq. in.]. The action, however, was only observable at the level of the upper surface of the liquid.†

"(4) The formation of spongy zinc is determined by the presence of foreign metals which produce an oxidation of the metal through electro-chemical action. Nahnsen has already proved many times that the zinc becomes spongy most readily when the solution contains such impurities as copper, arsenic, or antimony. In a 10 per cent. solution of zinc sulphate, which contained 0·004 per cent. of arsenic (as ammonium arsenite), a porous grey zinc was observed to form after one minute, and at the same time a distinct evolution of hydrogen was to be seen. The oxidation of the zinc, therefore, took place at the expense of the water of the solution.

"It should be here explained that the grey zinc sponge contains zinc, the crystallisation of which has been prevented by the absorption of oxygen; and the possibility of the co-operation of hydrogen need not therefore be altogether excluded. In any case, however, it is impossible to accept the view that such

* The precipitate contains nitrite and requires further investigation.

† At the place where the zinc, water, and air meet, hydrogen peroxide would always be formed.

substances as chlorine, iodine, hypochlorous acid, and the like prevent the formation of the grey zinc by decomposing a hydride of zinc,[*] which would otherwise be harmful; their action is to be ascribed solely to the fact that they are acid-forming agents. Our observations upon spongy zinc are therefore in exact agreement with the views of Nahnsen. If the interpretation of our experiments be correct, spongy zinc can never be separated from *acid solutions;* and as a matter of fact, it is never produced if care be taken that the zinc solution shall have an acid reaction. "The determination whether a zinc sulphate solution is neutral, acid, or basic appears to be of the greatest importance for purposes of electrolysis. It is well known that litmus is not available; and among the indicators which are capable of showing the presence of free acid in zinc sulphate, *Congo red* occupies the premier position. This colouring-matter, when in aqueous solution, is not altered either by the normal or by the basic sulphate of zinc, but is coloured blue by free acid.[†] The reaction is sufficiently sharp for most purposes, a want of sensitiveness being observable only in the estimation of very minute quantities of free acid. This colouring-matter, however, will not indicate whether a zinc sulphate solution is normal or basic; and to determine this point a titration experiment is necessary.

"We found in our experiments that in 10 to 50 per cent. solutions at 18° C., 10 grms. of zinc sulphate required 4 c.c. of a centi-normal soda solution to produce a distinct turbidity in half a minute. The salt was repeatedly re-crystallised with great care, at first from a very slightly acidified solution, and afterwards from water and alcohol. The behaviour of the salt towards centi-normal soda solution showed no change after further re-crystallisation, and its reaction may therefore be regarded as characteristic of the normal salt. The quantity of soda solution necessary is, of course, very dependent upon both the temperature and the degree of concentration. Thus, we used the following volumes of soda solution for every 10 grms. of zinc sulphate, in order to produce turbidity. The weights of zinc oxide corresponding to the soda used in each experiment are given in adjacent columns; the quantities of soda used (and equivalent zinc oxide) are calculated in the last two columns as per 10 c.c. of the solution.

* Siemens and Halske, *loc. cit.*
† The use of Congo papers is to be recommended; they can easily be prepared by allowing filter paper to absorb some of the Congo red solution. The colour of these papers changes like that of litmus paper but in an inverse sense.

Percentage of salt in the solution.*	Temperature.	Actually used per 10 grammes of salt.		Calculated as used for every 10 c.c. of the solution.	
		Centi-normal soda solution required.	Weight of zinc oxide equivalent to soda used.	Centi-normal soda solution required.	Weight of zinc oxide equivalent to soda used.
		c.c.	Milligrms.	c.c.	Milligrms.
50	18° C.	4	1·6	2·7	1·1
50	58°	14	5·7	9·4	3·8
50	68°	20	8·1	13·5	5·5
30	18°	4	1·6	1·5	0·6
10	18°	4	1·6	0·4	0·16
10	74°	14	5·7	1·5	0·31
10	80°	20	8·1	2·1	0 85
1	18°	12 to 15	5 to 6	0·15	0·06
1	80°	12 to 15	5 to 6		

The first appearance of the turbidity indicates that the solution of the sulphate of zinc has become more than saturated with oxide; and the centi-normal soda solution is therefore a very convenient means for ascertaining the neutrality of a solution, or for determining its acidity or basicity. The determination may be made by deducting the number of cubic centimetres of soda solution required to produce turbidity in a neutral solution from that actually employed to obtain the same effect in the liquid under examination. The method may be employed to test for very small proportions of acid, but is only approximately correct.

Concentrated solutions of normal zinc sulphate are therefore able to dissolve small quantities of zinc oxide; and the electrolysis of such solutions, even if extended over several hours, will produce a normal crystalline deposit of zinc; and the danger of obtaining grey spongy zinc is first met with when the solution has become basic owing to the oxidation of the metal. Very little acid is sufficient to prevent its formation; and so long as 10 c.c. of the concentrated solution of sulphate requires the use of 6 c.c. of the alkaline solution to produce the first sign of turbidity, the liquid is fit for use as an electrolyte; this is equivalent to 0·016 per cent. of free sulphuric acid. But the liquid must be kept thoroughly mixed, because, owing to the varying rates of migration of the ions, it is liable to become very much diluted at the cathode; and in dilute basic solutions the formation of a porous cathode deposit is of normal occurrence.

"If in spite of this method of procedure the formation of the grey deposit should take place after the lapse of a few hours, it will be found on isolated spots at which the mixing of the

* Percentage by weight.

solution is hindered, so that a dilute solution of low conductance is formed locally, and the free acid becomes neutralised at that point by the oxidisation of zinc. On this account zinc oxide may be precipitated. Such an action takes place, for example, in the capillary spaces, which are left between projecting crystals of zinc, and especially on the perpendicular edges of the hydrogen bubbles which cling to the zinc. At these places the formation of spongy zinc may be first observed in the form of small dark wart-like projections. The material forming these projections is full of capillary spaces, which contain a basic and very dilute zinc solution; the formation of spongy zinc is therefore facilitated, and it is not surprising that the black spots formed at the beginning rapidly increase until at last they cover the whole surface of the electrode.

" Finally, it must be remembered that the formation of grey zinc can only be avoided if a current density of at least 1 ampere per sq. dm. [0·0645 amp. per sq. in.] be used. This is quite in agreement with Kiliani's observation that the formation of oxide (and the evolution of hydrogen) is always more marked when the current density is low.

" The opposite extreme of *too high a percentage* of free acid in the solution is equally to be avoided in this process of refining; because the result would be a slow evolution of hydrogen at the cathode simultaneously with the deposition of zinc. It is true that under these circumstances the formation of grey zinc would be obviated, but the white and well-crystallised deposit that would result would be rough, since hydrogen bubbles remain clinging for a long time to the zinc. An early limit is thus set to the thickening of the layer of deposited metal. The presence of the free acid tends to promote the solution of impurities in the anode, an effect that is to be avoided.

" In order to obtain a solid and reguline deposit of zinc in *the process of refining,* a glass cell was used, divided into three compartments by diaphragms of silk cloth; for the anodes purified zinc was cast into the form of either round or square plates 1 cm. [0·4 in.] thick ; for the cathodes sheet zinc was used corresponding with the anodes in size and shape. The cathode solution in the central compartment was kept constantly agitated by means of mechanical stirrers, so that it was thoroughly mixed in contact with the whole surface of the cathode. Since the oxidisation of the zinc in the bath is practically constant, its effects could be neutralised by a continuous generation of acid in the bath itself. For this purpose a separate small platinum anode was introduced into the cathode compartment, and was connected with a second battery, so that a slight evolution of oxygen took place at its surface; the wire from the negative pole of this second battery was connected to the zinc cathode, after the manner diagrammatically illustrated

in Fig. 152. It was thus an easy matter to regulate the current strength in the subsidiary circuit in such a way that the acid should be generated at exactly the required rate, and that the acidity of the electrolyte should thus be maintained constant. Thus, for example, a current of 0·01 ampere would produce 0·43 grm. [6·6 grains] of sulphuric acid in 24 hours, and this would suffice for the neutralisation of 0·36 grm. [5·5 grains] of zinc oxide. Or, to avoid all possibility of rendering the cathode zinc impure by platinum, the use of the second circuit may be omitted, and the necessary quantity of acid may be added to the bath from time to time (at about 12-hour intervals). The quantity thus required for a total electrode surface of about 600 sq. cm. [93 sq. in.] would amount to about 0·2 grm. [3·08 grains] of sulphuric acid 24 hours; and this quantity would be distributed through about 1·5 litre [2·5 pints] of solution. The anodes, from which bubbles of hydrogen were seen occasionally to rise, were removed from the bath once every day in order that the impurities clinging to them might be brushed away. After they had been replaced the electrolysis proceeded as before. Any particles that might become detached were retained in the anode compartments by the diaphragms. No visible evolution of hydrogen was permitted at the cathode, and if any isolated bubbles of gas were observed they were removed by raising the electrode plate. The distance between the electrodes in our experiments amounted to several centimetres, the current density was at least 1 ampere per sq. dm. [0·065 per sq. in.] of cathode surface, and the slope of potential between the anodes and cathodes amounted to from 0·3 to 0·6 volt.

Fig. 152.—Connections with subsidiary electrodes in zinc deposition.

"It is advisable to deposit zinc on both sides of the cathode, because, otherwise, the separation of grey zinc may easily commence on the back. This arrangement has also the additional advantage that the number of the electrodes that may be introduced into a bath can be increased at will.

"The current density of 1 ampere used corresponded to a separation of about 29 grms. of zinc per sq. dm. [28·9 grains per sq. in.] in 24 hours, so that a layer about 0·4 mm. [0·016 in.] in thickness was deposited in the day. The electrolysis could be continued ordinarily for from two to three days without any formation of porous zinc. The cathodes became coated with a solid white coat of zinc which never exceeded 2 mm. [0·08 in.] in thickness. At the edges of the plates, however, the deposit was thicker, and it was here that, as the operation proceeded, rough patches and growths were formed, in which gradually small nests

of spongy zinc were found, and this was the sign that the cathode must be replaced."

No further remarks upon the work of Kiliani, and Mylius and Fromm need be made here, since it refers to the use of soluble (metallic zinc) anodes, and is, therefore, chiefly of interest in connection with electro-plating and electro-typing; and it will suffice to point out that in these two branches of electro-chemistry the current density usually ranges from 200 to 300, and in exceptional cases rises to 700 amperes per sq. metre [0·13 to 0·2, or 0·45 amp. per sq. in.], and often the electrolytes used have a *reducing* action. Reference will be made to some of the points observed in practical experience with these processes after treating of the third method of extracting zinc.

3. Electrolysis of Dissolved or Fused Zinc Salts with Insoluble Anodes.—Luckow's Process.—Luckow, in his patent,[*] to which attention has already been drawn, made several proposals in connection with the use of insoluble anodes, among which the introduction of a current of sulphurous acid into the electrolyte vat may be especially noted—a method of procedure that has been frequently re-discovered at a later date. Luckow, however, was not very fortunate in this use of sulphurous acid, inasmuch as he proposed to employ it as a means of converting into a harmless substance the chlorine that is evolved at the anodes when solutions of zinc chloride are being electrolysed. It must not be forgotten that the use of Luckow's deoxidising agent increases the acidity of the electrolyte at an enormous rate. Thus, whether the solution used be the chloride or the sulphate, whether, therefore, the group Cl_2 or SO_4 ($= SO_3 + O$) be liberated from the deposited zinc, the use of SO_2 to render these anions harmless will always be attended by the formation of a quantity of free acid, which is double that corresponding theoretically to the zinc precipitated, thus:—

$$SO_4 + SO_2 + 2H_2O = 2H_2SO_4$$
$$Cl_2 + SO_2 + 2H_2O = 2HCl + H_2SO_4.$$
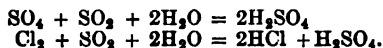
If, therefore, the liberated acid is to be neutralised by means of zinc ore, as specified in Luckow's patent, it is evident that after the first neutralisation two molecules of zinc salt will be contained in the liquid for every one that had previously been decomposed. Hence in a very short time it would become necessary to find some other means of neutralising the acid (the proportion of which is doubled at each operation) other than that of allowing it to dissolve zinc compounds. But, at the same time, the direct use of solutions which have been neutralised by means of the ores is not permissible in practice, owing to the quantity of impurities that are thus introduced into them. Although Luckow's process, as patented, has not been adopted on the large

* German Patent 14,256 (see p. 285).

scale, the specification contained some valuable suggestions to which reference will be made later. At present a short account will be given of a few of the best known among the numerous processes that have been patented.

The Létrange Process. — Létrange,[*] in numerous patent specifications, describes in general terms all the methods and conditions of work of a process for the treatment of zinc-bearing substances, excepting those which must be observed for the production of coherent zinc plates. The patent specification prescribes many details of work that are quite impracticable; and the process might have been left unnoticed here had not the accounts published in various technical journals and text books led to the belief that it was in actual use in zinc works. It cannot be disputed that Létrange has made practical experiments in the electrolysis of zinc on a large scale at his works in St. Dénis, but it is certain that if he obtained any practical result, it was not by following accurately the details of his patented process. According to this patent, "Zinc blende is roasted at so low a temperature, that very little sulphur is removed, most of the sulphide being converted into sulphate. The sulphate is dissolved in water, and decomposed by the electric current (a process which appears to be very simple on paper !), and the sulphuric acid thus set free serves to dissolve calamine and zinc oxide. For this purpose it is caused to flow through a system of masonry basins, which are connected with one another by pipes, and are filled with the zinc-bearing material. As soon as the first vessel is deprived of its zinc oxide, it is disconnected from the series, is re-charged, and is then again introduced as the last of the series. The solution saturated with zinc is conducted to a reservoir, from which it is usually led to the electrolysis vessel, which is placed at a somewhat lower level. In this reservoir the zinc solution may be purified (!) from foreign metals according to known methods. The silver and lead contained in the zinc mineral collects in the extraction-vats, and is therefore not lost. The electrolytic tanks are constructed of wood lined with lead, or of glass, cement, &c. and contain zinc (or copper or brass) plates as cathodes, together with carbon anode plates. The solution of zinc sulphate is introduced at the bottom of the vat, whilst the liberated sulphuric acid escapes freely at the same rate from the top on account of its lower specific gravity. The zinc separates at the cathode. If the zinc oxide to be treated should be very pure, the process is simplified because the solution may be effected in the electrolyte tank itself. In that case, either two vessels placed in communication are used, or else one vessel is divided into two compartments by a porous division. The one vessel

[*] German Patent 21,775. Austrian Priv. of Nov. 12, 1881, &c. [English Patent, 3211, July 22, 1881.]

(or compartment) serves to receive the anode and the zinc oxide or calamine, as the case may be, and the other contains the cathode on which the deposited zinc is separated. Since zinc oxide is a bad conductor of electricity, it is mixed with a certain proportion of carbon, in order to bring it into direct conducting communication with the anode, and so to facilitate solution."

In the whole of this description, discussion of the difficulties is simply evaded. They are lightly passed over, while the simpler matters are treated as broadly as possible.

Other Patented Processes.—In the same way there is a whole series of inventors who for the most part specify some method, usually well known already, for effecting the solution of the zinc contained in ores, metallurgical products or waste material; they then combine this method with the electrolytic treatment of the resulting solution, and the invention is complete. It will suffice to give the references in the accompanying footnote[*] to some patents of this description.

Squire and Currie[†] deposit the zinc as an amalgam by employing a cathode of mercury in an alkaline solution, and then distil off the mercury. This also is impracticable from the technical point of view.

Some other patentees utilise the anode energy. Thus, Siemens & Halske[‡] propose to use the same process for zinc blende that they introduced for the treatment of copper matte and sulphide of copper ores. But it has been found that when iron salts are present in the electrolyte, the deposition of good solid zinc at the cathode is impossible.

Currie[§] suggests the recovery of certain other metals in the form of insoluble chlorides at the anode, during the electrolysis of chloride of zinc solutions.

In C. Hoepfner's process[||] poor oxidised ores and metallurgical products are treated with solutions of caustic alkali, and the resulting solutions, after purification with zinc dust, are introduced into the electrolysis tanks. During electrolysis chlorates will be formed in the anode compartments where haloid salts of the alkalies and alkaline earths are present. The anode and cathode cells are separated by suitable (!) diaphragms. Such diaphragms are unquestionably necessary for the success of the process, but, unfortunately, no material that would be suitable for use with the proposed solutions has yet been found.

[*] Lea and Hammond, English Patent 10,868, Aug. 25, 1886; Croselmire, English Patent, 4,286, March 20, 1888; Burghardt, German Patent 49,682; Heinzerling, German Patent 64,435; Choate, U.S.A. Patents 512,361, 518,711, 518,732, &c.

[†] English Patent 12,249, Sept. 27, 1886.

[‡] German Patent 42,243 (see Chapter on *Copper*).

[§] U.S.A. Patent 466,720, Jan. 5, 1892. [English Patent 212, Jan. 5, 1892.]

[||] German Patent 62,946, 1891.

Lange and Kosmann * propose to obtain both zinc and sulphuric acid by the electrolysis of zinc sulphate solutions. For this purpose zinc blende is roasted ; the roaster gases are led into water containing roasted ore in suspension, and thus the electrolyte is produced. No details are given concerning the electrolysis itself.

Use of Deoxidising Agents.—At this point reference may be made to an investigation, to which allusion was made in the first edition of the book, but which the author has been unable as yet to begin, owing to the want of time and opportunity. Experience, alike in electrolytic analysis and in electro-plating, have shown that certain organic compounds are especially adapted for use as depolarising agents. Classen, in his work on *Chemical Analysis by Electrolysis*, recommends the use of oxalic acid in combination with the oxides of the metals to be deposited, and accompanied by alkaline oxalates. In electro-plating, tartaric and oxalic acids, cyanides, and other organic substances have been employed with special advantage. The organic matter contained in these substances is usually sacrificed, being in most cases oxidised to carbon dioxide, &c. But it is always possible to select an organic compound, with intermediate products between the initial and the final stages of oxidisation, and to interrupt the process at a moment when the oxidisation has not proceeded so far as to render the material worthless. Among the substances most suitable for this purpose are the distillation products of coal-tar. The author has generally used the so-called liquid carbolic acid, or mixture of cresols, which remains after the removal of the more volatile carbolic acid. Nevertheless, other organic compounds may also be available. The cresol cannot be used as such, inasmuch as it is insoluble, or only very slightly soluble, in water, and is, moreover, a very bad conductor of electricity. But its conversion into a soluble compound is a problem which presents no difficulty. When an alkaline solution of the substance may not be used (it dissolves readily in caustic soda or potash) the cresol is digested with strong sulphuric acid, and is thus readily converted into cresol-sulphonic acids, which, either as such or in the form of salts, fulfil the two conditions necessary for good electrolytes, high conductance and easy solubility in water. After sufficiently long continued electrolysis these sulphonic acids are oxidised completely at the anode into carbon dioxide, water, and sulphuric acid, but by interrupting the electrolysis at suitable moments the whole series of intermediate products that are theoretically possible may be produced. There can be no doubt that a number of oxidation processes for organic compounds may be combined with electrolytic methods for the extraction of metal with great advantage to both. It may, indeed, be assumed that such a

* German Patent 57,761. [English Patent 8716, June 5, 1890.]

procedure could be adopted with reasonable safety in all cases in which peroxides, in conjunction with acids, permanganates, chromic acid, arsenic acid, and other compounds or mixtures used generally in aqueous solutions, have hitherto been employed. The division of the cost of electrolysis between two final products, taken in conjunction with the reduction of the electromotive force required for the deposition of zinc, are again advantages of the highest order, which should be as acceptable to the organic chemist as to the metallurgist.

Use of Depolarising Agents.—The next group of patents is concerned with the discovery of suitable depolarising media mainly for the anode. In certain respects these methods may be classified with those just described; but they differ from them in that the products of the work at the anode are not utilisable or are worthless.

Coehn* has recently proposed to use lead accumulator plates as anodes for the electrolysis of oxygen salts, such as zinc sulphate, and when they have become thoroughly peroxidised on the surface, to utilise them for the generation of electricity in lead peroxide—sulphuric acid—carbon elements. But no account has yet appeared of the practical application of this method.

Pertsch† electrolyses mixtures of haloid salts with oxalates. The use of oxalic acid or oxalates has long been known in connection with Classen's analytical processes in which they have been very successfully applied, but they would be too costly for technical work.

Cassell and Kjallin ‡ effect the electrolysis of zinc sulphate solutions in a cathode compartment with porous walls, using an iron anode in a solution of sulphate of iron. The use of diaphragms, however, introduces difficulties (as already explained), whilst no solid zinc deposit can be obtained in presence of iron.

To prevent the formation of spongy zinc Siemens & Halske § recommend the use of weak solutions of halogens, or of hypochlorous or hypobromous acid, and similar halogen compounds, because these inventors attribute the production of the sponge to the formation of hydride of zinc at the cathode, and so would oxidise the hydrogen by means of these added substances, which, as above remarked, are only used in very small proportions.

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* German Patent 79,237, 1893. [NOTE.—In Coehn's English Patent 23,478, Dec. 6, 1893, it may be noted that the use of lead *cathode* plates is recommended when oxygen is being prepared electrolytically. Hydrogen is absorbed by the lead until the metal is saturated and the gas is freely evolved. The plates are then renewed, the hydrogen plates being employed as the positive plates in a galvanic battery in place of zinc. A combination of the two processes might be more feasible than that in the text.—TRANSLATOR.]

† German Patent 66,185.

‡ German Patent 67,303; and English Patent 21,193, Nov. 22, 1892.

§ German Patent 66,592. [English Patent 12,731, July 11, 1892.]

The patent specification contains only the assertion, but no proof, of the existence of a hydride of zinc. The author does not believe in the hydride hypothesis, but agrees rather with the views of Mylius and Fromm on this point, and can indeed corroborate them, for he has obtained the same result as Siemens & Halske by the use of reducing agents such as sulphurous, phosphorous, and hypophosphorous acids in the cathode compartment.

Lindemann's Process.—So also the substance recommended for use by Lindemann* is anything but oxidising, yet it is capable of giving very good results unless its residue, after prolonged use, should render the bath too impure. It consists of precipitated zinc sulphide suspended in the electrolyte during the time of electrolysis. The conditions to be observed in practice are minutely described in the patent specification, the more important portion of which is here translated :—"A concentrated aqueous solution of zinc sulphate of 37° to 38° B., which corresponds to about 50 per cent. of $ZnSO_4 + 7H_2O$, is used. This solution must be freed, if necessary, from any metal that is capable of being precipitated by metallic zinc. It is placed in a cubical lead-lined wooden vat, which afterwards serves as an electrolytic tank. Here it is treated with hydrogen sulphide until it is saturated with the gas, whereby a considerable precipitate of the insoluble white sulphide of zinc is produced ; and this, after a time, sinks to the bottom. As soon as the volume of the precipitate ceases to alter, and the latter occupies about $\frac{1}{4}$ to $\frac{1}{3}$ of the total contents of the tank, the supernatant acid liquid is drawn off and neutralised with such bye-products from smelting processes as contain zinc oxide, as, for example, with zinciferous furnace accretions, or flue dust. It must not be overlooked, however, that objectionable constituents may thus be added to the solution, and these must be separated by means of metallic zinc before use, because the purity of the electrolytically deposited zinc is dependent upon that of the zinc sulphate solution employed. Small proportions of iron, manganese, nickel and cobalt sulphates, however, exert no prejudicial effect during electrolysis, and are without influence upon the quality of the zinc obtained.

"A neutral solution of zinc sulphate of the above concentration is then added to the precipitate of zinc sulphide, which must always be present in sufficient quantity in the tank; and this precipitate is distributed uniformly through the liquid by stirring. The cathodes, which are cut from rolled sheets of refined lead, are then suspended in the bath so prepared by means of small leaden strips attached to them, which serve to make contact with the electrical conductor. The anodes are made from stronger leaden plates, about 4 mm. [0·16 in.] thick,

* German Patent 81,640, 1894.

and are connected to the positive pole of the dynamo. They are placed about 10 cm. [4 in.] apart, and in the space between them, about equidistant from each, hang the thinner leaden cathodes, connected with the negative pole. The edges of the cathode sheets are painted over with asphalte varnish before suspending them in place, so that the zinc deposit may be conveniently removed after it has attained a thickness of 1 to 1·5 mm. [0·04 to 0·06 in.]. Later, the deposited zinc plates, trimmed uniformly at the edges, are substituted for the leaden cathodes.

"During electrolysis the precipitate must be kept constantly in motion in the bath, which is best done on a large scale by the circulation of the solution ; for the quality of the deposited zinc is mainly dependent on the zinc sulphide suspended in the liquid. The anodes in this process are gradually converted on the surface into lead peroxide, which would scale off in the baths if they were not removed from the tanks from time to time, washed with water, and freed from the loose dark layer of oxide. They are ultimately replaced by new lead plates.

"As already explained, the finely divided sulphide of zinc in the liquid has a marked effect on the character of the separated metal, and causes it to deposit in a good solid form ; it does not, however, prevent the bath from becoming gradually more and more acid with sulphuric acid as the electrolysis proceeds, until at last a limit is reached at which no further quantity of zinc can be deposited, because the action of the main current of electrolysis is weakened by the polarisation in the cell.   This point is reached when the electrolyte contains 54 to 56 grms. per litre [5·5 to 5·6 per cent. or 3850 to 3900 grains per gallon] of free acid (H_2SO_4), with a current density of 108·5 amperes per sq. metre [0·0694 amp. per sq. in.]. Before this extreme limit is attained, however, all the cathodes are lifted out of the bath and immersed in water, in order to purify them from solution, and from the adherent zinc sulphide.   The acid liquid is run off into a separate reservoir in order to allow the precipitate to settle, and the tank is then re-charged with neutral zinc sulphate and with zinc sulphide, and after re-introducing the electrodes the current is passed anew.

"During the electrolytic process there is a gradual decomposition of zinc sulphide in the bath owing to the action upon the sulphide of the free acid that is generated ; but no notable quantity of hydrogen sulphide escapes into the air, at least, not in sufficient quantity to be prejudicial to the health of the operators.   The precipitate, at first, alters in its physical properties, becoming yellowish in colour, and, at the same time, denser and heavier, so that it subsides more rapidly to the bottom.   On continuing the electrolysis all the zinc sulphide will become used up, leaving a dirty yellow film of sulphur on the surface of the bath.   The formation of free sulphur is

explained by the circumstance that during electrolysis with insoluble anodes, some active (ozonised) oxygen is always produced at the positive electrodes, which is partly used up in converting the lead of the anode into peroxide, and partly in decomposing the hydrogen sulphide produced from the sulphide of zinc, and thus causing a separation of sulphur.

"Fresh sulphide of zinc must, therefore, be added to the bath from time to time, or else the zinc sulphate solution, which is slightly acid at first, may be electrolysed only so long as corresponds to the resistance of the zinc sulphide to the acid which is liberated in the solution. The point at which the action must be stopped may be determined by leading hydrogen sulphide into a 50 per cent. solution of zinc sulphate. In this case precipitation of zinc sulphide ceases when the filtered solution contains about 18 grms. of free acid per litre [1260 grains per gallon]. This corresponds (in round numbers) to about 12 grms. [840 grains per gallon] of zinc; consequently, 12 kilogrammes of zinc may be obtained electrolytically from 1 cb. metre [¾ lb. per cb. ft.] of a neutral solution, which is mixed with zinc sulphide, before it becomes necessary to change the solution. But if the process be allowed to proceed further, at least three times this quantity may be reduced from 1 cb. metre (of course at the expense of the zinc sulphide), since according to the above, the maximum limit of acidity is reached with 56 grms. per litre. If the second alternative be decided upon, it is necessary to have a sufficient reserve of zinc sulphide always at hand. This may conveniently be made from weaker solutions, such as result from the extraction of residues containing but little zinc; only in that case the liquid must be purified before use by contact with metallic zinc in order to effect the removal of any small quantities of injurious metals of the hydrogen sulphide group that may be present.

"Chemical analysis of the deposited zinc fails to show the presence of any foreign substances, excepting, perhaps, a little zinc sulphide which has been retained mechanically, and which might have been removed by more thorough brushing and washing. This circumstance should add to the profitableness of the process when applied on a large scale. The current density, as already indicated, should be 108·5 amperes per sq. metre." [0·07 amperes per sq. in.]

Nahnsen's Experiments.—The patents still remaining for discussion seek to remove the difficulties which stand in the way of the production of dense deposits, by the regulation either of the current, of the manner of applying the current, or of the temperature; and by obtaining as pure an electrolyte as possible, or by submitting it to brisk agitation.

Nahnsen,* in the first place, found that when the temperature

* German Patent 56,700.

of the electrolyte was low, the current density employed must
be smaller. The advantages of working with low current
densities may thus be attained by cooling the electrolytic
solutions; for the zinc deposit varies according to the following
table :—

Amperes.		Temperatures of solutions.			
Per sq. metre.	Per sq. in.	0°	10°	20°	30°
10	0·0064	Solid.	Incipient sponginess.	Spongy.	Spongy.
50	0·0323	,,	Spongy.	Incipient sponginess.	Spongy.
100	0·0645	,,	Solid.	Spongy.	Incipient sponginess.
150	0·0968	,,	,,	Solid.	Spongy.
200	0·1290	,,	,,	,,	Solid.

Further experiments, however, have led Nahnsen to alter his
opinions on this subject; and the statement of his later views
may be taken from a subsequent [British] specification,* in
which he writes that the double sulphates of zinc and alkali
metals, proposed by Herrmann, permit the use of lower current
densities than do the simple zinc salts, which had been referred
to in the earlier patent. The conductance of the double salts
is, however, said to be less than that of the single salts by reason
of their inferior solubility. Again, in these double salts the
zinc forms a constituent of the anion, and so (accompanied by
two SO_4 groups) finds its way to the anode, while the zinc
deposited at the cathode is reduced by secondary action. This
peculiarity of the double salt has in practice led to very unsatis-
factory results, which render the regular working of the elec-
trolysis in the baths almost impossible.

"When a soluble anode is employed for the purpose of separat-
ing or refining metals, a solid salt is formed at the anode even
at a very low density of current, and, finally, the passage of the
current is interrupted. When using a solution of simple
sulphate of zinc at a concentration of 30° Beaumé, and a current
having at the anode a density of 418 amperes per sq. yard
[0·32 amp. per sq. in.], no crystallisation takes place, but when
employing a concentrated solution of sulphate of zinc and
ammonia the formation of zinc is already observed with a
current of 63 amperes per sq. yard [0·048 amp. per sq. in.].
The reason of this chemical process is, that in the last-mentioned
salt two equivalents of sulphate of zinc go to the anode.

* German Patent 71,155. [English Patent 2913, Feb. 15, 1892.]

"When employing an insoluble anode the conditions are still more complicated. When electrolysing sulphate of zinc alone it is decomposed into Zn and SO_4, the latter forming sulphuric acid by combining with the water and giving off one atom of oxygen; this sulphuric acid being specifically lighter than sulphate of zinc rises to the surface. A double alkaline salt, for instance sulphate of potash and of zinc, is, under ordinary circumstances, decomposed by electrolysis into K and $ZnSO_4$. SO_4, so that even when employing an insoluble anode an agglomeration of sulphate of zinc is formed at the same whereby the nascent free acid is drawn to the bottom. The slightest changes in the concentration of the electrolyte, on which changes largely depends the quality of the zinc belonging to the anion or the cathion, influence this process, and the practical result of the latter is, that part of the nascent acid rises to the surface, but by far the greater portion of the same sinks to the bottom. Even the best regulated and best conducted circulation is at length insufficient to prevent the stated inconvenience. A remedy may be found in employing very diluted solutions, but there the conductivity is so much decreased that no sensible advantage is secured.

"Now I have ascertained by experiments that the decomposition of the double salts of sulphate of alkali and zinc is influenced by the temperature in the same measure as by a dilution of the electrolyte—a fact, the probability of which was also indicated by the theory. It is possible to ascertain experimentally the changes in the decomposition from degree to degree. Between 104° and 122° F. [40° and 50° C.] the point is reached at which the decomposition of the double salt into the simple salt is completed. In practice I prefer to employ a temperature of 122° to 140° F. [50° to 60° C.], and I obtain thereby with perfect security a decomposition taking place in the same manner as when simple salts are used; and all the nascent acid, as in the latter case, rises to the surface. . . . Notwithstanding the character of a double salt being completely wanting in the electro-chemical sense, the relation between the density of the current at the cathode and the deposit of zinc has remained the same, and it is thereby clearly shown that it is not the quality of the electrolyte of being a solution of a double salt which is the first condition for the employment of currents of low density, but only the partial or complete secondary reduction of the zinc by the primary alkali.

"Having ascertained these facts by experiments I still improve the electrolyte by reducing the proportion of zinc, or of sulphate of zinc, in the same, as far as the intended density of the current permits. Thus I employ a very diluted solution of sulphate of zinc containing but $1\frac{3}{4}$ to $2\frac{3}{4}$ ozs. of crystallised sulphate of zinc per litre [$\frac{1}{2}$ to $\frac{3}{4}$ lb. per gallon] according to the density of the current, and enrich this solution with sulphate of

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alkali—I may also, but with less favourable result, employ sulphate of magnesia—of which I take as much as will be dissolved at the temperature at which it is to be used, or, for practical reasons, at a temperature about 18° F. [10° C.] below the first. The electrolyte which I employ contains 1¾ to 2¾ oz. of crystallised sulphate of zinc and 10½ to 5⅜ oz. of sulphate of alkali per litre [3 to 1¼ lbs. per gallon] according to the density of the current."

Using condensing engines, Nahnsen states that he is able by this process to extract 1 ton of zinc from its ore at an expenditure of from 3 to 3½ tons of coal, according to the calorimetric value of the fuel. In one experiment, conducted at a temperature of 92° C., and with a current density of 100 amperes per sq. metre [0·064 amp. per sq. in.], the deposit of zinc was not spongy, even though bubbles of steam were formed at the cathode.

Nahnsen's views concerning the action of electrolysis in the experiments which he has described in his patent specification may be allowed to remain as they are expressed above. But the fact may be brought into prominence that persulphate of zinc is formed at the anode when the current density reaches 500 amperes per sq. metre [0·32 amp. per sq. in.].

Coehn's Process.—Coehn* seeks to prevent the evolution of hydrogen (?) at the cathodes which gives rise to spongy deposits when low current densities are used, by interrupting the current from time to time. Thus, with a density of 50 amperes per sq. metre, a solution of zinc sulphate should give a more solid deposit if the current be broken about 50 times to the minute. In order that the time during which the current is interrupted may not be wasted, a continual alternation of the current between two sets of baths may be effected by means of a mechanical switch.

Cowper-Coles' Process.—Cowper-Coles,† considering that an irregular current favours the deposition of solid deposits, starts the electrolysis with a current of 500 amperes per sq. metre [0·32 amp. per sq. in.], but at intervals of eight minutes he increases the density of the current very considerably. Moreover, he maintains zinc dust in suspension in the electrolyte. His process is intended for electro-plating with zinc ("galvanising"), and it is quite evident that it would be impossible to introduce zinc dust into the vats in the extraction of zinc from the ore ; but the suggestion is noteworthy, because it affords additional evidence that the formation of zinc sponge may be prevented by the application of a reducing agent.

Hoepfner's Process.—Hoepfner, in conclusion,‡ seeks the solu-

* German Patent 75,482, 1893.
† German Patent 79,447, 1894. [*Cf.* English Patents 21,760, Nov. 14, 1893 ; and 7145, April 10, and 19,797, Oct. 17, 1894.]
‡ English Patent 13,336, July 8, 1894.

tion of the problem of obtaining solid deposits by the use of rotating cathodes. In this way a brisk movement may be maintained in the electrolyte, so that any tendency to separation in the solution may be obviated. A chloride solution is used as electrolyte. For the recovery of the chlorine, porous cells must be arranged as anode compartments between the cathodes. Such arrangements have undoubtedly proved satisfactory, but they are wanting in novelty.*

[The Ashcroft Process.—This process has been devised mainly for the treatment of the Broken Hill ore (New South Wales), which contains about 25 to 30 per cent. of zinc, and 26 to 30 per cent. of lead, both as sulphides, with 20 to 30 oz. of silver per ton, and for which no satisfactory process has yet been found. An account has been given by Swinburne,† from which it is explained that the finely divided ore is to be roasted sufficiently to convert the bulk of the zinc into oxide, without endeavouring to perfect the calcination, as it is cheaper in this instance to waste a portion of the zinc than to push the roasting to completion. The roasted ore is then leached with a solution containing ferric salts with sulphate and chloride of zinc. In this way the oxide of zinc in the ore exchanges places with the dissolved persalt of iron, so that ferric hydroxide separates and is allowed to settle, whilst a soluble zinc compound is formed. Lead sulphate—the product from the roasting of lead sulphide—would remain almost insoluble. The solution of zinc is then conveyed to the vats containing metallic zinc plates or shavings, upon which all the silver in the solution should be deposited by simple exchange. After this it is transferred to the (wooden) electrolyte tanks, which are divided into two by a porous partition of close-textured canvas. Three tanks are used in series; in the first two crude wrought-iron anodes are used, so that for each equivalent of zinc deposited in the cathode cell an equivalent of iron is dissolved at the anode. It is to prevent the passage of this iron into the cathode chamber that the porous division must be employed, and the level of the liquid in the latter division is higher than that in the anode cell. In the third cell carbon anodes are employed, and at these the ferrous salts formed in the earlier compartments are peroxidised, so that the cathode solution may be used to leach another batch of ore. It is necessary that all the iron shall be peroxidised, as ferrous oxide would not be deposited in the leaching vats, and for this reason it is generally preferred to carry the cathode reactions so far that a small proportion of hypochlorite may also be present. Sheet-zinc cathode plates are used, and the sponginess of the deposit is said to have been overcome by the use of a solution containing basic salts of zinc, which are inevitably produced in

* Cf. *Zinc Refining* on p. 286, *et seq.*
† *Journ. Soc. of Arts*, 1896, vol. xliv., p. 820.

the leaching of an excess of zinc oxide with a solution of normal zinc salts. About one-third of the zinc present in the solutions is deposited during one passage through the electrolysis house. Zinc sulphate dissolving as such from the calcined ore, and certain impurities, such as alumina and manganese salts, tend to accumulate in the solution; and to prevent this a certain proportion of the liquid is allowed to run to waste after each operation, an equal volume of sea-water being added in its place. No hint is given in the paper as to the current density or other conditions that are recommended. It remains to be seen whether the process may prove successful in spite of the complications introduced by the necessity to obtain complete precipitation of iron during the leaching of the calcined ore, superadded to the difficulties involved in the use of partitions in the electrolyte cells, and in obtaining a good reguline deposit of zinc.—TRANSLATOR.]

Modern Industrial Developments.—The matter collated in the above account does not include all that has yet been published in relation to the interesting and important question of the commercial extraction of zinc by electrolysis. Of the remaining points, some will be mentioned within the next few pages, whilst many may be passed over as having no importance from a technical point of view. Nevertheless, an examination of many of these latter proposals might lead to the discovery of useful matter, which, at the right time and in the right place, could be applied with good effect.

The author is unable to record the results of work on a large scale. It is, however, only after lengthy experiments, extending over some years, that electrolytic zinc extraction has been started at Duisburg on a large scale at the works of Sicilia and Siegena, and these works are unquestionably still engaged in extensive experiments. Hoepfner, also, is constantly experimenting at Jührfuhrt on the Lahn. And the construction of a third plant—that of E. Mathes and Weber at Duisburg—has still not advanced beyond the plan stage. It is, therefore, at present, unreasonable to expect published descriptions of processes which have been worked out at such cost. The following remarks are therefore based on the accounts which have been recorded earlier in this Chapter, together with the results of observations that the author has himself made, but that, for various reasons, have not previously been published.

Conditions for the Electrolytic Extraction of Zinc.— Enough has already been said above concerning the electrolytic treatment of zinc alloys, and especially of the zinc crusts of the Rössler-Edelmann process for the desilverisation of work-lead.

At the present time interest is mainly centred in the treat-

ment of zinc-bearing pyrites, and of the residue from such material after it has been roasted for the manufacture of sulphuric acid, and in the working of galena mixed with blende. These raw materials could not well be treated by the usual metallurgical processes of roasting and distillation. The roasted zinciferous pyrites was almost useless, since it could not be employed in iron smelting, owing to the quantity of zinc and sulphur that remained in it; whilst the blende and galena, so far as the mixture could not be separated by dressing, yielded its zinc in the form of sulphate, which is an almost unmarketable product.

The Solution of the Zinc.—In treating the residues from burnt zinc-bearing pyrites, they should be subjected to a sulphating or chloridising roast. Richer zinc ores are not treated electrolytically at present. Even in chloridising roasting the formation of sulphates is unavoidable; but, if it be desired to electrolyse chloride solutions, a satisfactory and cheap medium for the conversion of zinc sulphate into the chloride is found in the calcium chloride liquors of the ammonia-soda process, the calcium of this solution becoming converted into sulphate by the exchange. For an account of the method of conducting the roasting process, and of the plant required, reference must be made to the handbooks on this subject.

Purification of the Solutions.—The zinc solution obtained by one or other of the above methods is rendered as nearly neutral as possible by the addition of oxide or roasted zinc ores, or zinc residues. The waste materials from the zinc works are especially suitable for this purpose, as they contain metallic zinc, which is capable of changing places with several metals that cannot be precipitated as oxides by oxide of zinc. Zinc dust is recommended for the purpose, and its use has even been patented; but it cannot generally be regarded as a cheap reagent. When the solution is neutral, or slightly basic, it may still contain iron in the form of ferrous salt; and this metal can only be extracted if the ferrous salts be peroxidised into the ferric state. Larger quantities of iron may be extracted by the method (the originality of which is somewhat doubtful), which was patented by the *Aktiengesellschaft (formerly) Egestorff's Salzwerke*,[*] and which consisted in blowing a current of air through the solution after adding calcium carbonate to it. If the solution contain the zinc in the form of chloride the iron may be oxidised and precipitated by the addition of chloride of lime; the calcium chloride which remains in the solution having no prejudicial effect on the subsequent process. When only a small percentage of iron is present it may be most readily precipitated by the addition of soda, or zinc oxide, or carbonate, mixed with a chromate solution; the oxide of chromium, produced by the

[*] German Patent 23,712.

reduction, is separated along with the ferric hydroxide, thus :—

$$6FeCl_2 + 2Na_2CrO_4 + 4Na_2CO_3 + 12H_2O$$
$$= 3Fe_2(OH)_6 + Cr_2(OH)_6 + 12NaCl + 4CO_2$$
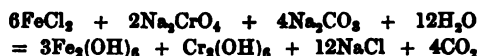
Pfleger * recommends for the precipitation of foreign metals the use of basic zinc salts ($ZnCl_2 . 3ZnO$, or $ZnSO_4 . 4ZnO$) which he obtains by the solution of zinc oxide in neutral salts. This medium is very suitable if, as already pointed out, ferrous salts have been previously peroxidised, otherwise iron would not be precipitated. The liquid, after purification in this manner, is passed through a filter press, and may then be used at once as an aqueous solution ; or it may be evaporated to dryness, if the chlorides are to be electrolysed in the fused and anhydrous condition. A lead-lined wooden vat is used as a precipitating tank ; the evaporating pans may consist of large iron vessels lined with lead.

The Apparatus and Conditions for Electrolysis.—These depend primarily upon the nature of the salt, and secondarily upon whether an aqueous solution or a fused salt is to be treated, and, finally, upon the manner in which the anode reaction is to be utilised.

The electrolytic vessel may be made of wood, or of wood lined with lead, for the electrolysis of aqueous solutions. The vessels themselves are either rectangular tanks, or if diaphragms are to be used, they may consist of frames with the diaphragms placed between them, constructed after the pattern of the filter press.

The apparatus shown in Figs. 153 to 156, in simple form, has been used by the author for experiments in which the use of diaphragms was necessary. It consists of a number of frames, R, which are held together by means of a screw-press working in a horizontal plane, and which thus forms a single vat, divided up into narrow compartments by sheets of parchment paper or other suitable partitions. A frame of this description is shown in Figs. 153 and 154, which give, first, a vertical section along the line A B (Fig. 153), and then a horizontal section through C D (Fig. 154).

The wooden planks, S, S, u, form the side and bottom walls of the tanks, and are 70 to 80 mm. thick by 120 mm. wide [$2\frac{3}{4}$ to $3\frac{1}{8}$ in. by $4\frac{3}{4}$ in.]. The top is covered with a strip of wood 15 to 20 mm. thick by 75 mm. wide [$\frac{1}{2}$ to $\frac{3}{4}$ in. by 3 in.]. In Fig. 154 this is shown surmounted by a copper strip, M, the width of which is equal to the thickness of the wooden lath. By placing O and M a little out of the middle line of the frame, space may be left for the admission of even thick electrodes. At each end of the copper strip, M, is fastened a round metal rod with a

* U.S.A. Patent 495,637, April 18, 1893.

thread cut in such a manner that the frames may be held together by the screws G. One of these rods is made of such length that a slot may be cut in the end projecting beyond the screw thread to take a wedge - shaped metal key, W, which is attached to the conducting wire. The other end of the wire is provided with a similar wedge by which contact is made with one of the electrodes in the next

Fig. 153. (Section.)
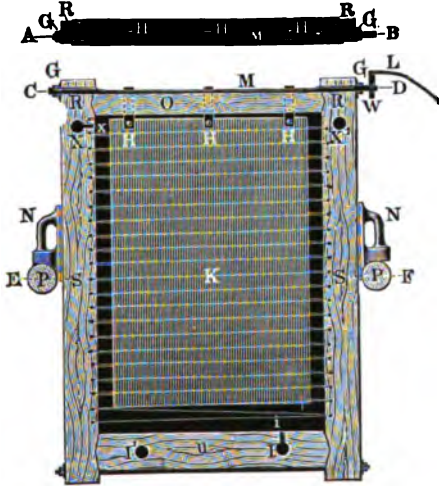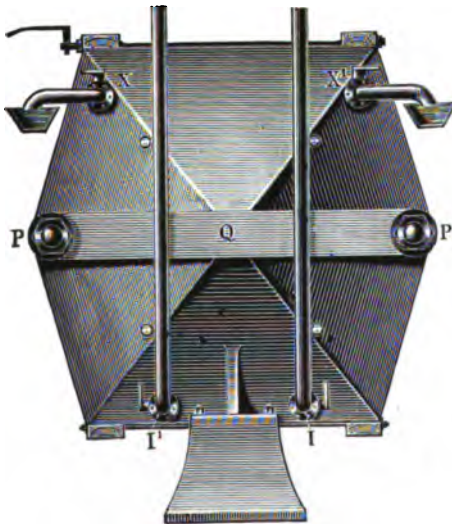
Fig. 154.

Fig. 155. (End elevation.)
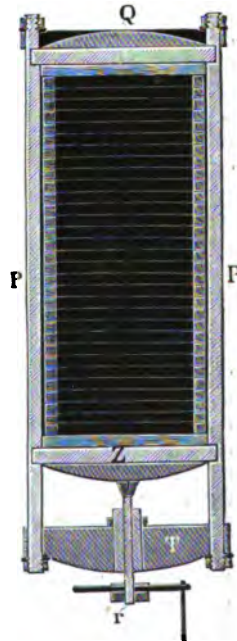
Fig. 156. (Plan.)

Apparatus for electrolysis of zinc solutions.

bath. Each frame contains four apertures, and these, when

all the frames are joined up together, unite to form four channels, I, I¹, X and X¹, running lengthwise in the bath. From the ducts, I and X, narrower passages, *i* and *x*, lead into the cathode compartments, whilst similar passages form means of communication between I¹ and X¹ and the anode cells. The electrolyte is introduced into the cathode cell through the channel I, and flows away through X; and the channels I¹ and X¹ serve for a similar purpose in connection with the anode compartment. Fig. 154 shows a cathode plate, K, suspended from three metal bands, H. The cast-handles, N, are screwed on to the sides of the frames, so that they serve not only as handles, but as supports, resting on the round iron bars, P, which are about 100 mm. [4 in.] in diameter. These rods are carried through the frame of the press, Q and T (Fig. 156), and are fastened in it by screws. The frames themselves are pressed together by the screw and hand-wheel, *r*, and the pressure plate, Z, which also rests on P. Fig. 155 shows an end view of the pressure-plate, Q.

It should be unnecessary to explain that the electrolyte may, if desired, be circulated through the various anode, or cathode, compartments successively, instead of simultaneously, the channels in the wooden frames being then, of course, cut to correspond with the new arrangement. Numerous modifications of this apparatus have been patented, but nearly all the details in most cases are devised after the model of the well-known osmosis apparatus of the sugar-refinery and the newer forms of filter press. The description of the above apparatus is given, less by way of recommendation than as an illustration of the principle. Whenever possible electrolysis should be conducted without the use of diaphragms, and this is easily accomplished if fused zinc chloride be operated upon, the separated chlorine being recovered.

The forms of apparatus,* constructed by the author for the electrolysis of fused zinc chloride for the recovery of zinc and chlorine, are shown in Figs. 157 and 158. Fig. 157 represents an experimental apparatus for use with a current of 100 to 150 amperes, whilst Fig. 158 shows one intended for use on a large scale. In each figure, B is a leaden vessel of circular cross-section, G is a trough completely surrounding the apparatus, and intended for the reception of cooling water. K is the cathode formed of zinc plate, connected to the conducting wire, N; the method of cutting this cathode to the required shape will be explained subsequently. U is a circular groove on the rim of the vessel to receive the cover, D, and seal it in place. The anodes, A, are carbon rods held either by a single clamp, V,

* This apparatus, as well as that described in the Chapter on *Sodium* (pp. 72-75), has been patented with the author's sanction in most civilised countries by the firm of Fr. Hornig, of Dresden and Taucha-Leipzig.

Fig. 157.—Borchers' zinc-extraction apparatus (experimental).
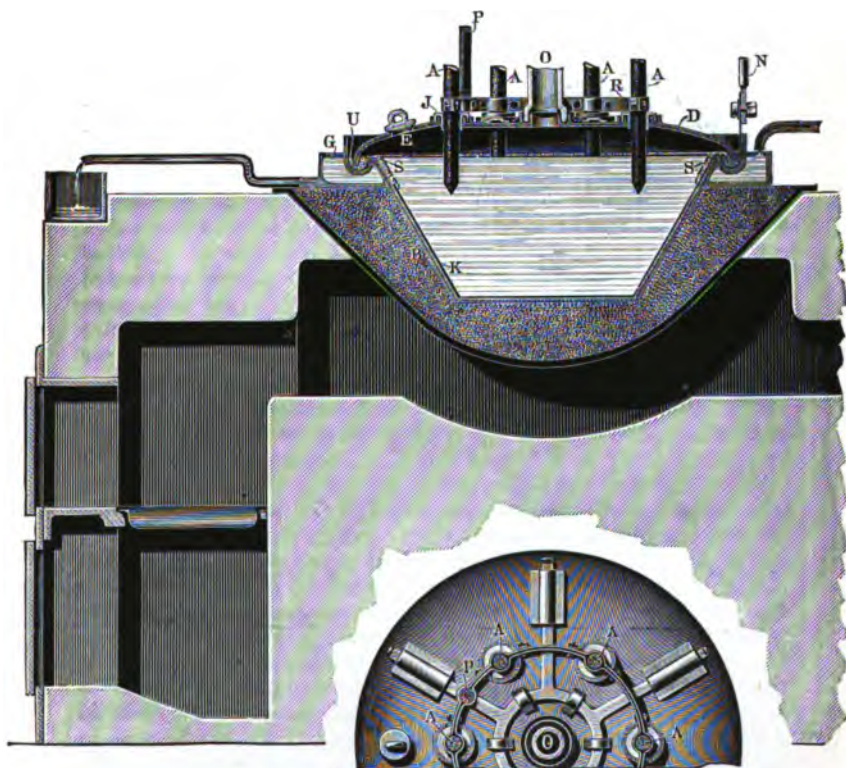
Fig. 158.—Borchers' zinc-extraction apparatus for use on large-scale
(Section; and view of part of cover from above).

when only one carbon is used, as in Fig. 157; or by a ring-shaped grip, R, common to all the anodes as in Fig. 158; the clamps, V or R, make connection with the conducting wire, P. The insulating rings, J, are only required for the larger vessel, which has a leaden cover; the lid of the smaller apparatus is made of fireclay. The leaden vessel stands in an iron trough filled with sand; this latter substance serves both to equalise the heat during the first stage of external firing, and to minimise the loss of heat by radiation during the subsequent internal heating by means of the electric current.

In use, zinc chloride is first melted in the apparatus in such quantity that the vessel, B, is filled up to the groove on the rim, the zinc cathode, K, is then introduced, and the cover, D, is placed in position. The cover is suspended so that it does not rest quite on the bottom of the groove, and water is then run into the outer trough, G; the effect of this is to cause the solidification of the salt, S, in the groove and on the upper rim of leaden vessel, and the cover is thus sealed firmly in position. Electrolysis is now commenced, and if a high current density, such as 1000 amperes per sq. metre [0·645 amp. per sq. in.] of cathode surface be employed, sufficient heat will be generated to enable the use of external firing to be almost dispensed with. In the larger apparatus

Fig. 159.—Shape of zinc plate to be cut for use as cathode.

only so much fire need be held on the grate as will ensure that the apparatus does not become chilled, and the damper in the flue may be left with only a narrow passage open, whilst the door of the ashpit is completely closed. The smaller apparatus rests on a cylinder of sheet iron over a triple burner. During electrolysis the zinc becomes deposited upon those portions of the cathode that are not covered by solidified salt, while the chlorine escapes through the opening, O. Zinc chloride is added from time to time through another opening, E, in the cover, so that the level of liquid in the vessel may be kept constant. When the zinc has been deposited in sufficient thickness, the flow of cooling water in G is stopped, so that the salt in the groove may become fused, the cover is lifted off as soon as it is thus loosened. A fresh cathode is introduced after removing that which has been coated, and electrolysis is continued as before. The shape given to the thin zinc sheet for the cathode is shown in Fig. 159. Cut in this way it may be easily bent to the required form, and a strip of zinc or of copper may be soldered to the extension piece for the purpose of making contact.

[Lorenz * has also proposed the electrolysis of fused chlorides of silver, lead, cadmium, and zinc, as a means of separating these substances independently from their mixed ores, by a system of "fractional electrolysis." In passing a current of moderate density through such a mixture, silver (practically alone) was first deposited, then much lead with little zinc and cadmium, then diminishing proportions of lead and increasing quantities of the remaining metals, and, last of all, pure zinc.]

Electromotive Force and Current Density.—The various investigators are agreed in the statement that the current density must usually be much higher in the electrolysis of zinc than in the separation of other metals from dissolved or fused compounds. In using aqueous solutions of zinc salts, a current of less than 100 amperes per sq. metre cannot well be used, whilst in some processes the minimum is 200 amperes, and the density may range from this up to 700 amperes per sq. metre ; at the same time in such solutions the E.M.F. must be nearly 3 volts for a current of 200 amp. per sq. metre. The treatment of the fused chloride, however, is far more economical, since the E.M.F. then usually ranges from 3 to 4 volts if the current density amount to 1000 to 2000 amperes per sq. metre [0·65 to 1·3 amp. per sq. in.] of cathode surface, and even if that at the anode be considerably higher. Such a voltage would be exceeded in aqueous electrolytes with a current density of 500 amperes per sq. metre. The use of molten zinc chloride appears therefore to present many advantages over that of aqueous solutions of the salts of the metal. With equal expenditures of energy, it is possible to deposit in the former instance in a small apparatus *as much zinc as would be obtained from 5 to 10 larger forms of apparatus* treating aqueous solutions. Moreover, the *chlorine is recovered without the use of diaphragms.* The resulting zinc may be melted together without loss, and possibly could even be rolled out direct, if long trough-shaped vessels with a V cross-section were used.

The Prevention of Spongy Zinc.—As practical re-agents for the prevention of spongy zinc in aqueous electrolytes, reducing substances and weak acids in the cathode compartments with the application of currents of suitable density, have proved successful. An intermittent increase in the strength of the current over that normally used, and a frequent interruption of the current have equally contributed to the satisfactory formation of thick deposits of zinc.

Utilisation of the Anode Reactions. — In electrolysing aqueous solutions, it is possible to effect the oxidation or chlorination of organic compounds, for the production of which the peroxide of lead (or of other metals) has previously been

* [English Patent 25,074, Dec. 24, 1894. *Cf. Zeitschr. für Elektrochem.*, 1895-6, vol. ii., p. 318.]

used. The production of persulphates * and the recovery of chlorine have also been accomplished under these conditions. In the electrolysis of the fused chloride, chlorine is the only bye-product that may be obtained.

Cost of Zinc Extraction.—No statements as to the actual economical results of applying a chloridising or sulphating roast to the ores have yet been published. The power required for the separation of zinc, using insoluble anodes, amounts to from 3 to 4·5 H.P. hours per kilogramme of zinc [1⅓ to 2 H.P. hours per lb.]. No trustworthy statements concerning the other ex-penses in connection with a large installation have yet appeared.

The Uses of Zinc.—The zinc is obtained from metallurgical works in the form of cake or dust; and these are used in silver works for the desilverisation of work-lead, in chemical works as a reducing agent, in the foundry for the production of house-hold implements, architectural ornaments, and alloys, and in electro-technics for the electrodes of galvanic batteries. It has a very extensive use in the protection of iron ("galvanised iron"). The sheet rolled from zinc serves as a roofing material, and is used both in the household and in building, as well as for printing plates (in photo-zincography), &c.

The zinc compounds are obtained for the most part as bye-products in the treatment of zinc-bearing ores and metallurgical products from the working of other metals. The metal forms the starting point only in the manufacture of zinc white.

CADMIUM.

Properties and Occurrence of the Metal.—Cadmium (Cd; atomic weight = 112; specific gravity = 8·6 to 8·7) is a very white and lustrous, soft, malleable metal of crystalline (regular) structure. It fuses at 320° C., and boils at 800° C.

In the molten condition it alloys very readily with most other metals; and of its alloys, those with bismuth, lead, and tin (Wood's, Rose's, and other "fusible metals"), are the best known, mainly on account of their low fusing points.

At the normal temperature, cadmium may remain for a long time unaltered in dry air; but at higher temperatures it burns even more readily than zinc, to which metal it is very closely allied in its chemical properties. It dissolves with ease in the more important inorganic (sulphuric, hydrochloric, and nitric) acids, forming salts, which are derived from the oxide, and are very soluble in water. The oxide and hydroxide are capable of dissolving in solutions of alkaline hydroxides, forming salts, derived from the hydroxide, but having the cadmium in the acid radical. Cadmium is precipitated from its salts by zinc and by more electro-positive metals.

* Elbs and Schönherr, in *Zeitschrift für Elektrochemie*, 1894, 1895.

Cadmium almost always accompanies zinc in nature; the Silesian calamine, and blende are especially rich in cadmium carbonate and sulphide respectively. The last-named compound (Greenockite) is very rarely found alone.

Extraction of Cadmium.—Its extraction is nowhere made the sole object of a metallurgical process. The metal is always obtained as a bye-product in the extraction of zinc. In the reduction of roasted zinc ores it occurs as the first product of distillation, and is chiefly found mixed with varying proportions of zinc, in the second (or iron) condenser. This deposit, which is generally coloured more or less brown by the oxide of cadmium, is repeatedly reduced and redistilled, the first portions condensed always containing the largest proportion of the cadmium. When these have been sufficiently purified for zinc, they are cast into rods, and sent thus into commerce. The apparatus employed is similar to that used in the extraction of zinc, but the retorts are usually smaller and made of cast iron, since clay is too porous to retain the vapour of cadmium sufficiently well.

The **Electrolytic Production and Refining of Cadmium** require scarcely any description, as they are conducted under practically the same conditions as in the case of zinc. According to the experiments which the author has tried on a small scale, it would seem that the electrolysis of cadmium salts should be simpler than that of zinc compounds, for the current densities of 60 to 150 amperes per sq. metre [0·04 to 0·1 amp. per sq. in.], which give an unsatisfactory deposit of zinc, are capable of yielding a good and useful deposit of cadmium. There is no record of the electrolytic method of treating this metal having been employed in practical work.

Uses of Cadmium.—Cadmium is mainly used for the production of very fusible alloys. The compounds of cadmium are for the most part made from the metal, either direct or after solution, the haloid salts being used in photography, and the sulphide as a pigment.

CHAPTER V.

MERCURY.

Properties and Occurrence of the Metal.—Mercury or quicksilver (Hg; atomic weight = 200; specific gravity = 13·5) is a bluish-white metal that is fluid at ordinary temperatures, the freezing point being −39·4° C., and the boiling point 360° C. Mercury acts as a solvent for most metals (gold, silver, lead, bismuth, tin, zinc, cadmium, alkali and alkaline earth metals). The alloys of mercury are known as amalgams.

Pure mercury is unaffected by the air at low temperatures, but at about 300° C. it becomes oxidised to the red oxide. Ozone and the halogens unite with it at ordinary temperatures. The metal dissolves readily only in nitric acid and *aqua regia* among the common acids. Two series of compounds are known—the mercurous (protoxide) compounds, of which the type is Hg_2O, and the mercuric compounds, corresponding to the type of HgO. The sulphide also forms thio-salts, in which the mercury occurs in the acid radical.

Small quantities of native mercury are found, but the metal generally occurs as the sulphide, HgS, in Cinnabar, and less frequently as the subchloride, Hg_2Cl_2, in Calomel (or horn quicksilver), and other compounds.

Extraction of Mercury.—Mercury is extracted almost exclusively from cinnabar. Rich ores are treated in retorts, poor ores in shaft furnaces, often by mixing them with some material (lime, limestone, iron, &c.) capable of absorbing sulphur, and submitting them to a combined process of roasting and distillation. The mercury vapours, escaping from the furnace, are condensed in systems of tubes and chambers. The greatest loss occurs in working the poorest ores. The condensed metal is purified partly by filtration, partly by distillation.

It has often been proposed to substitute electrolytic methods for the somewhat wasteful and unhealthy smelting processes for treating mercurial ores. The direct electrolysis of the ores would, however, present the same difficulties that are met with in the treatment of copper, zinc, or lead ores; and if electricity is to find an application in this field, it will be by chemical solution of the mercury, followed by electrolytic separation. At present, however, few results have been obtained. It is noteworthy that cinnabar is readily soluble in solutions of alkaline sulphides containing hydroxides of the alkali metals, and that the mercury may be precipitated quantitatively by the electrolysis of such a solution. As yet, the method devised by Vortmann* has only been applied to analytical purposes. Should it ever be introduced on a commercial scale, much that is written in the Chapter on *Antimony* will be applicable here.

Uses of Mercury.—In the metallic state mercury is used very largely for thermometers, barometers, and other scientific apparatus. In the "amalgamation processes" it is extensively employed for the extraction of gold and silver from their ores, and it also serves for the intermediate formation of alkali metal amalgams in the electrolytic processes for producing alkaline hydrates.† The alkali metal amalgams are largely used in other chemical processes. Mercury is also employed in some of the so-called "anti-friction alloys." Other amalgams are used in

* A. Classen, *Quantitative Analyse durch Electrolyse*, Berlin, 1892.
† See *Alkali Metal Alloys*, p. 67.

the manufacture of mirrors, and as fillings for teeth in dental surgery. Finally, the metal is generally the starting-point for the manufacture of nearly all the mercury compounds employed in the chemical industries. The sulphide (vermilion) and the oxide are pigments; mercuric chloride is a valuable germicide; and fulminate of mercury plays an important part as a primer in connection with explosives.

CHAPTER VI.

T I N.

Properties and Occurrence of the Metal.—Tin (Sn; atomic weight = 118; specific gravity = 7·3) is white, but has a faint yellowish shade; it is a very weak metal, but is soft and exceedingly tough. It is most malleable at about 100° C., becoming somewhat brittle at 200°. It melts at 228° C., and boils between 1450° and 1600° C., but tends to vaporise more or less at lower temperatures. Fused tin dissolves most other metals very readily, and frequently forms valuable alloys with them.

Tin resists the action of the atmosphere well, but when heated it burns readily in air. It unites with the halogens at the ordinary temperature, and when melted it combines with sulphur, phosphorus, arsenic, and antimony. Among the commoner acids, hydrochloric acid is the best solvent for tin; sulphuric acid attacks it but slowly, whilst nitric acid oxidises it to a hydroxide of the formula $SnO(OH)_2$, which is known as stannic acid. Tin may thus be found in salts, sometimes in the acid radical, and sometimes in the base; in the former case the salts may be regarded as having been derived from the hydroxides, $Sn(OH)_4$ or $SnO(OH)_2$. The remaining tin compounds are derived either from protoxide, SnO (stannous compounds), or from the binoxide, SnO_2 (stannic compounds). The stannic sulphide, SnS_2, also forms thio-salts. In nature, tin occurs mainly as oxide (SnO_2) in tinstone or Cassiterite, which is very commonly associated with wolfram (tungstate of iron and manganese). Other tin compounds are so rare that they need not be referred to here.

The Extraction of Tin from its Ores.—Only one process is practically employed, and this consists in the direct reduction of the oxide by smelting, usually after some mechanical preparation. The high specific gravity of the tinstone renders the dressing of the ore a simple process, unless wolfram be present, in which case separation is difficult owing to the specific gravities of the two minerals being nearly identical. When large proportions of wolfram are present, this substance (or at least the

tungstic acid, WO_3, in it) must be removed prior to smelting, since tungsten compounds give trouble in the smelting of the tin. The separation of tungsten, however, is very simple, and, if rightly effected, may even be made remunerative; the method employed is described in the Chapter on *Tungsten.* The ore, freed from tungsten, is mixed with fluxes suitable for any gangue stuff that may remain, and is reduced in low blast-furnaces or in reverberatory furnaces. The crude tin which results from the reduction is liquated and refined, and thus affords a product sufficiently pure for general use.

The Electrolytic Treatment of Tin Ores.—Burghardt [*] has proposed a method for the electrolytic treatment of tin ores, but as it is unpractical in character, it will suffice to give the reference to the original patent. Vortmann and Spitzer's [†] process is but little better. This consists in melting finely pulverised tin ore mixed with from two to three times its weight of a mixture of one equivalent of sulphur and two equivalents of soda. Air is excluded during the fusion, which results in the formation of a thio-stannate; this salt is then washed out, the solution is allowed to settle, after the addition of ammonia and ammonium sulphate, and the clear liquor is electrolysed with insoluble (lead-plate) anodes. The first part of the operation, although easily accomplished in the laboratory, is with difficulty effected on the large scale. Vessels such as would be employed in the latter case will not retain the melted material, and fusion in the reverberatory furnace is accompanied by a heavy loss of tin and a considerable expenditure in repairs to the furnace. The second part of the process, even if it should be industrially successful, could scarcely be protected by the patent as it was described by Classen [‡] several years previously. The direct electrolysis of tin ores is impossible by any of the processes hitherto attempted.

The Electrolytic Treatment of Tin-plate Scrap.—The treatment of tin-plate scrap by electrolysis has become a question of considerable importance. Two objects have to be attained—first, the tin must be separated from the iron and re-deposited in a convenient and useful form; and, secondly, the iron must be so completely cleansed from tin and lead that it may be utilised in iron works.

The process patented by Beatson [§] would be very costly in operation. He encloses the scrap metal in cylinders made of iron wire mesh, and suspends these as anodes in a boiling solution of caustic soda to which potassium cyanide has been added. By way of cathode there may be used either iron plates, slowly rotating rollers, which consolidate the somewhat loose deposit of metal, or the walls of an iron vessel. The inventor, however, has

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[*] German Patent 49,682.   [†] German Patent 73,826.
[‡] A. Classen, *Quantitative Analyse durch Elektrolyse,* 1892 (Berlin).
[§] English Patent 11,067, Sept. 18, 1885.

evidently discovered that potassium cyanide is unstable in boiling aqueous solutions, for, in a later specification,* he relinquishes the use of this substance and is content to employ an alkaline hydroxide solution as electrolyte. The deposit of tin thus obtained from the alkaline solution is refined electrolytically in a solution of a tin salt, the tin being deposited on rollers which rotate in contact with one another so that the tin may be obtained in a dense form.

Price† also has patented the use of alkaline hydroxide solutions as electrolytes, whilst Fenwick‡ has used solutions of stannous chloride. Smith§ has described an installation put down by Siemens & Halske according to an older patent of Gutensohn's.|| In this case the tin-plate scrap contained from 3 to 9 per cent. (averaging 5 per cent.) of tin, and was electrolysed with the aid of a solution of sulphuric acid or of sulphates, yielding ferrous sulphate and iron liquors in addition to metallic tin. A Siemens O_{18} dynamo, absorbing 8 H.P., was used, and afforded a current of 240 amperes at 15 volts. Eight cells were employed, made of wood 50 mm. [2 in.] thick, lined with india-rubber to the thickness of 3·5 mm. [⅛ in.], and placed at a height of 1 metre [39·4 in.] from the ground. The internal dimensions were 1500 mm. in length by 700 mm. in width by 1000 mm. in depth [5 ft. × 2 ft. 3½ in. × 3 ft. 3½ in.]. On each side of the vats was placed a tank in which were dissolved the cuttings that had been stripped of tin; after solution had taken place the liquid was concentrated in pans placed at a lower level, and, finally, the ferrous sulphate was crystallised in tanks sunk beneath the ground level.

The scrap was packed with great care, neither too closely nor too loosely, in strong baskets composed of wooden bars, the internal dimensions of the frames being 1200 mm. in length by 300 mm. in width and 850 mm. in depth [4 ft. × 11¾ in. × 2 ft. 8½ in.], and the contents of each basket weighed from 60 to 70 kilogrms. [130 to 150 lbs.]. Small strips of tin plate were inserted in the mass of cuttings at the time of packing, and these, projecting above the frames, were utilised as conductors for the current. The charging and emptying of the anode baskets were effected twice daily. The cathodes consisted of tinned copper plates 1200 mm. long by 950 mm. wide by 1·5 mm. thick [4 ft. × 3 ft. 1½ in. × 0·06 in.], and two cathodes, together with one anode basket, were placed in each electrolyte cell. The edges of the cathode plates were strengthened by copper strips of square section, and the plates were allowed to

* English Patent 12,200, Aug. 5, 1890.
† English Patent 2119, Jan. 25, 1884.
‡ English Patent 8988, July 9, 1886.
§ *Journ. Soc. Chem. Ind.*, 1885, vol. v., p. 312.
|| German Patent 12,883.

rest in grooves at the sides of the tanks, placed at the distance of 100 mm. [4 in.] from the anode frames. Both the anode baskets and the cathodes were provided with india-rubber rollers to prevent injury to the rubber lining of the vat; and both anodes and cathodes could be raised from, or lowered into, the electrolyte by means of cranes. The solution was made up at the beginning of the experiment by mixing 1 volume of sulphuric acid (of 60° B.) with 9 volumes of water.

With a current of 240 amperes a total deposition of about 4·25 kilogrms. [9·35 lbs.] might be expected per hour, but, as a matter of fact, only about half this was obtained, a large proportion of the current being expended in the solution of iron and the deposition of hydrogen. After use for seven weeks the electrolyte became saturated with iron, and was then treated for the recovery of the ferrous sulphate. The whole of the tin was not allowed to dissolve in this way; but after the scrap had been used as anode for from five to six hours it was transferred to the sulphuric acid vats, where the iron was readily and completely dissolved, the residual tin being left unattacked. Three or four workmen were required to handle 3 tons of tin-plate scrap per week.

From this account it may be gathered that the current density used was not very high. In each of the eight baths coupled in series a current of 240 amperes and 1·9 volts was employed; and as only those cathode surfaces that were turned towards the anode could be concerned in the electrolysis, the available cathode area (on the electrodes) was evidently 2 × 1·2 × 0·95 = 2·28 sq. metres [24·5 sq. ft.], and the current density was therefore but little more than 100 amperes per sq. metre [0·0645 amp. per sq. in.]. The use of 15 volts for the eight vats, or nearly 1·9 volts per vat, would, under these circumstances, appear to be somewhat excessive. The published account makes no mention of the method employed to work up the tin slime, which must inevitably be produced in this process.

By the treatment of 6 tons of scrap [per week], which is the maximum output from vats of this size, there would be obtained about 28 tons of crystallised ferrous sulphate, in addition to metallic tin, which might be sold as such or after conversion into tin salts. It is doubtful whether the former material would even repay the outlay on the sulphuric acid used, seeing that it is produced as a bye-product in many other metallurgical works, and is thrown upon the market at an exceedingly cheap rate. But it is evident from Smith's statement that if it were intended completely to strip the tin from the iron by electrolytic means, an enormous quantity of the latter metal would be dissolved with it. The author's own experiments point to the conclusion that it is impossible to remove the whole of the tin from iron when an acid solution is employed. Hence any use for the

waste product other than the unprofitable manufacture of ferrous sulphate is precluded.

In the preceding record of patented processes, the use of alkaline hydroxide, and especially of caustic soda, is referred to several times. It is well known that tin dissolves readily and without the aid of electricity, in warm solutions of caustic alkalies, hydrogen being evolved at the same time. Iron however, is almost entirely insoluble in such solutions, but becomes superficially oxidised as soon as it is exposed freely at the anode; hence the use of this electrolyte offers special advantages. The author can only record the results of small-scale experiments in this direction. Several works have adopted the method for the further treatment of the tin, which was described in the earlier [German] edition of this work.

Initial experiments with solutions of sodium stannate gave no satisfactory results, as it was found that a separation of stannic oxide in the bath led to an early interruption of the process. A 12 to 15 per cent. solution of common salt, to which 5 per cent. of sodium stannate had been added, proved to be far more successful, provided it was kept distinctly alkaline. But since alkaline hydroxides are able to dissolve tin even in the absence of an electric current, the bath tends to become richer in stannite. Hence the treatment is commenced with sodium chloride solution mixed with a few parts per cent. of caustic soda, which latter becomes converted into stannate as the action proceeds. At the outset the E.M.F. required is very low, and tin dissolves practically unaided if the solution be warmed to 40° to 50° C. But as the surface of the scrap begins to lose its coating of tin, the current density per unit area of the remaining tin increases, and the power absorbed becomes higher in consequence, the E.M.F. rising at the end of the process to 3 volts, even when a low current density is employed (calculated upon the cathode area, which remains constant throughout). The difference of potential between the electrodes at the commencement of the work is much lower than 3 volts, even when the current density amounts to several hundred amperes per sq. metre of cathode surface. In the experiments that were made the necessary E.M.F. averaged 1·5 to 2 volts per bath when the current density did not exceed 150 amperes per sq. metre [0·1 amp. per sq. in.], and provided that the current density was reduced to one-half by joining in parallel two baths, which had been charged at the same time, as soon as the bulk of the tin had been dissolved from the anodes.

The final products of this process are iron, tin, and a small quantity of "preparing salt" (mordant). The iron remaining in the anode basket is so pure, that it may be applied to any purpose for which good sheet iron scrap is used.

In order to utilise the tin, the spongy deposit is first washed

and pressed or dried in centrifugal machines, and may then be worked up into "tin salts." For the preparation of this salt, as pure a tin as possible is generally employed, and the chemical and physical properties of electrolytic tin render it especially suitable for the purpose. But if no sufficient demand should be found for the large quantities of tin salts that would be produced by the treatment of tin-plate scrap after this manner, it would become necessary to melt up the tin for sale in the metallic form. Several critics have stated that this latter alternative method is impracticable, but they have probably confused the problem with that of treating electrolytic zinc sponge. In other processes, the task of uniting electrolytic tin deposits by fusion has not proved by any means insuperable.

As concerning the third product, "preparing salt": it has already been explained that the original electrolyte (sodium chloride solution containing caustic soda), gradually becomes enriched with oxides of tin, since at first more tin is dissolved than is deposited. The alkaline reaction that is absolutely necessary for the process is maintained by the addition of caustic soda; and hence in the end a solution is obtained which, on evaporation, would afford a mixture of salts similar to the "preparing salt" of commerce. Any stannite that may be present could be oxidised by evaporation and calcination, if necessary with the addition of sodium nitrate. The preparing salt of the dyer is a mixture of sodium stannate and sodium chloride, obtained by mixing stannic chloride with caustic soda, and calcining the mixture of salts resulting from the reaction of the two.

The advantages of the last-named method of treating the scrap may be shortly summed up as follows :—

1. Complete stripping of the iron, which may therefore be used as sheet-iron scrap.

2. Recovery of pure tin, free from iron.

3. The possibility of using iron vessels, and of employing them as cathodes.

4. The possibility of constructing the anode baskets of iron, which is a very durable material for the purpose.

The Uses of Tin are very numerous. In the form of pure metal and as a coating on other metals (tin-plate, or tin on iron) it is used very largely for utensils of household and general use. It also plays an important part in many valuable alloys (bronzes, bearing metals, solders, &c.). The foil, which formerly consisted of sheet tin rolled very thin, is now usually lead, coated with tin, obtained by rolling plates of the two metals together. Most of the compounds of tin, which are chiefly used as pigments (mosaic gold, tin oxide, &c.) are prepared from the metal.

CHAPTER VII.

LEAD.

Properties and Occurrence of the Metal. — Lead (Pb; atomic weight = 206; specific gravity = 11·4) is a bluish-grey lustrous metal, exceptionally malleable, but of very low tenacity; it may be easily cut with the knife, rolled into plate, or pressed into wire. It melts at 330° C., and boils at a white heat, but becomes vaporised to a marked extent even at a red heat. When fused, it is a good solvent for other (especially the noble) metals.

At the ordinary temperature, lead resists chemical action well. It is true that it oxidises superficially either in air or in water, but the film of oxide or carbonate (for carbonic acid is never absent from natural water or air) protects the metal beneath it from further attack. Similarly sulphuric and hydrochloric acids act only upon the surface of the metal, by reason of the insolubility of the salts that are formed. Nitric acid, however, dissolves lead readily, forming the nitrate, which is soluble in water. Many organic acids, also, such as acetic acid, form easily soluble salts with lead in the presence of oxygen (air). Lead forms two simple oxides; the oxide, PbO, and the peroxide, PbO_2. A hydroxide is also known, connected with the former. Red lead or minium, Pb_3O_4, is a compound oxide ($= 2PbO + PbO_2$). With sulphur, lead forms only one important compound, lead sulphide, PbS, which combines readily with other sulphides forming lead mattes. Among lead salts, those which originate from the oxide contain the metal in the base, while those (plumbates) in which the lead forms part of the acid radical are derived from the peroxide or its hypothetical hydrate, plumbic acid, H_4PbO_4. Thus minium may be regarded as a lead plumbate having the formula Pb_2PbO_4.

Native lead does not occur in nature. The most important of its ores is **Galena**, PbS, and next to this is **White Lead Ore** or **Cerussite**, $PbCO_3$. Among the rarer minerals are:—**Anglesite**, $PbSO_4$, **Pyromorphite**, $PbCl_2 . 3Pb_3(PO_4)_2$; **Crocoisite**, $PbCrO_4$; **Wulfenite**, $PbMoO_4$; and **Stolzite**, $PbWO_4$. In lead works only the first two of the above-named minerals are used, together with a number of intermediate and waste products of metallurgical and other works.

Extraction of Lead.—Apart from special preliminary processes which are unavoidable when certain other metals (especially zinc) are present, the treatment of lead ores consists in obtaining first a crude metal, the so-called work-lead, which is then subjected to a refining process in order to obtain soft or market-lead. The work-lead is obtained either by roasting reactions, by reduction, by roasting and reduction, or by a precipitation process. The refining is effected either by oxidation after fusion, or by electrolysis.

1. The Reaction Process of Smelting.— Principles of Process.— When oxidised ores or products are melted with sulphides in proportion corresponding to the equation

$$2PbO + PbS = 3Pb + SO_2,$$
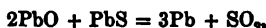
the lead contained in each is obtained, whilst the sulphur escapes in combination with oxygen as sulphur dioxide. If, for example, cerussite and galena had to be treated, it would only be necessary to smelt them together in the proportion indicated by the above equation, in order to obtain the lead from them. Sulphide ores, however, may be treated alone if a portion of the lead sulphide be first roasted to oxide or sulphate, the residual unaltered sulphide serving then as the reducing agent, whilst at the same time it yields its own lead in the metallic state. This process is based upon the three equations :—

(1) $2PbS + 7O = PbO + PbSO_4.$
(2) $2PbO + PbS = 2Pb + SO_2.$
(3) $PbSO_4 + PbS = 2Pb + 2SO_2.$
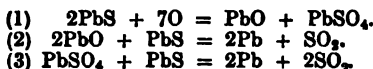
Variations in the purity of the ore, in the character of the lead required, in the cost of fuel, and in the labour demanded, have of necessity given rise to corresponding variations in the manner of smelting. Several processes may thus be distinguished:—

The Carinthian Process.—In this process small furnaces are used and small charges, and the temperature is kept as low as possible, so that after roasting is complete, the reaction indicated in the third equation of the last paragraph may take place. But in practice the roasting operation cannot be so accurately conducted that for every molecule of PbS remaining over exactly one molecule of $PbSO_4$ shall have been produced; and at the end of the operation there is usually an excess of sulphate and oxide, which have been produced according to the equations :—

$$2PbSO_4 + PbS = 2PbO + Pb + 3SO_2.$$
$$3PbSO_4 + PbS = 4PbO + 4SO_2.$$
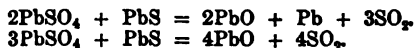
This lead is recovered, after sprinkling carbon upon the hearth of the furnace, by heating and thoroughly rabbling the residue. In this way the sulphate is reduced to sulphide, and this substance, together with the excess of carbon, effects the reduction of the oxide. Among the advantages of this process may be

enumerated the slight loss of lead by volatilisation, the small. quantity of residual matter which contains but little lead, and the purity of the lead extracted. The disadvantages, on the other hand, are the great consumption of fuel, and the heavy demands upon labour. The residue from the furnaces contains from 3 to 9 per cent. of lead; it is enriched by dressing to 50 to 60 per cent., and is then re-smelted.

The English Process.—Large quantities of ore are smelted in large furnaces, whilst a high temperature and oxidising conditions are maintained. The roasted products find a reducing agent in the large excess of sulphides present at the outset; and. the reduction of lead according to the equations given above is found to commence even with the introduction of the charge. When, from time to time, the process is checked by the formation of easily fusible slags, the charge has to be cooled, and the slag is thickened, if necessary, by the addition of lime. The advantages of this process are the low charges for fuel and labour; and the disadvantages are a considerable loss of lead by volatilisation, necessitating the use of a costly condensing plant, and the production of a residual slag, which is rich in lead and has to be re-smelted in special furnaces, and of an impure lead.

The Tarnowitz Process.—Large charges are roasted at low temperatures in large furnaces and then fused; this, therefore, is a combination of the English and Carinthian processes. The advantages of this method of working are found in the slight volatilisation of lead, the pure lead obtained, and the small outlay necessary for fuel and labour. But the disadvantage is that the residue contains much lead, which must be separated in special furnaces. These three processes, however, are only suitable for non-silicious ores. Lead silicate is not completely decomposed by the usual reducing agents, but it is readily formed during the smelting process by the direct union of silica and oxide of lead, as well as by the action of silica upon lead sulphate, thus:—

$$PbSO_4 + SiO_2 = PbSiO_3 + SO_2 + O.$$

The decomposition of the lead silicate by means of other metallic oxides, in order to obtain the easily reducible lead oxide, is not possible in reverberatory furnaces.

The French or Brittany Process.—This process aimed at treating silicious ores by slightly varying the Carinthian method of operating. But in almost all the works in which it has been tried it has been given up in favour of the roasting and reduction process.

The Ore-Hearth.—The ore is mixed with fuel, and is roasted and reduced in the ore-hearth, which resembles the smith's fire in its construction. In this case the roasted material is reduced partly by the residual unaltered ore, and partly by the carbon

of the fuel. The heat efficiency and the yield of metal are
both unsatisfactory, and a further disadvantage is that the
lead vapours escaping from the open hearth are very pre-
judicial to the health of the workmen.

2. **The Reduction or Roasting and Reduction Process.**—
Principles of the Process.—Oxidised ores and furnace products
may be submitted to direct reduction in places where they are
not in demand as additions to a sulphide charge; in this case
the process is one of simple reduction. Sulphide ores must first
be calcined as completely as possible, and any sulphates pro-
duced should be decomposed by silica, according to the equation
given on p. 327. The calcination is followed by the decomposi-
tion of the lead silicate by lime and ferrous oxide, an operation
which is carried on simultaneously with the reduction of the
resulting lead oxide by carbon :—

$$PbSiO_3 + CaO = CaSiO_3 + PbO.$$
$$2PbO + C = 2Pb + CO_2.$$
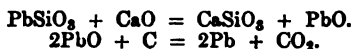
The calcination is effected in heaps, reverberatory furnaces, or
kilns, according to the nature of the ore; but the decomposition
of the lead sulphate by silica is only accomplished satisfactorily
in reverberatory furnaces, and is not attempted with poor lead
ores, or with those containing silver, copper, or zinc. The
calcination of poor ores (with less than 10 per cent. of lead) in
reverberatory furnaces is too costly. If silver were present, a
not inconsiderable proportion of this metal would be volatilised
at the high temperature necessary for the decomposition of
the lead sulphate. When copper is present, so much sulphur
must be left in the ore that there may be sufficient during
the subsequent smelting process to combine with all the copper
and carry it into a matte in the form of sulphide. Hence
it is unnecessary to eliminate the whole of the sulphur during
calcination; and if lead sulphate were present it would be
reduced to sulphide during the smelting, according to the
equation :—

$$PbSO_4 + C_2 = PbS + 2CO_2,$$
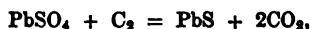
and this would react with the copper or copper compounds to
form regulus of copper, thus :—

$$PbS + Cu_2 = Cu_2S + Pb.$$
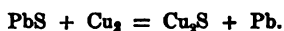
Zinc must be removed by leaching out the soluble zinc
sulphate after roasting, and prior to smelting, as it leads to
great irregularities and loss of metal in the blast furnace, both
on account of the difficulty of fluxing it, and by reason of its
volatile character, which gives rise to the formation of deposits
in the furnace, and to an increased loss of other metals in the
vaporous condition. The production of zinc sulphate in the

calciner is only possible at temperatures far below that at which
lead sulphate would be decomposed.

The discovery in New South Wales and Colorado of extensive
deposits of lead ore (mainly galena) containing silver, together
with considerable proportions of zinc blende, has led to the
invention and patenting of many processes for the treatment of
such ores. Of these a large number have not stood the test of
practical use, and the few that have any prospect of being
ultimately employed upon a large scale are based upon the
method that has been used for a long time in the Hartz and
Saxon works for the treatment of zinc-bearing galena. These
processes are conducted in six stages:—(1) Calcination at a low
temperature, with partial conversion of zinc sulphide into
sulphate; (2) completion of the conversion of zinc oxide into
sulphate by treatment of the calcined ore with sulphuric acid
or with sulphur dioxide and air; (3) leaching out of the zinc
sulphate; (4) treatment of the zinc sulphate solution for the
recovery of the zinc sulphate crystals or of zinc; (5) treatment of
the residue from the leaching vats for work-lead; (6) desilverisa-
tion of the work-lead for the extraction of silver and the
recovery of market-lead. Concerning other proposed methods
there are not yet sufficient data published to enable an accurate
judgment to be formed.

The calciners at present employed for the ordinary ores are
usually **long reverberatory furnaces**, in which the ore is
carried forward progressively from end to end, so that the action
is continuous and the furnace economical of fuel. Thus, whilst
the ore in the furnace is constantly worked forward in the
opposite direction to the flame, fresh charges of raw ore are
introduced as required at the end most remote from the fire-
grate; and the calcined material is removed in a pasty condition
at a point near the fire-bridge. Ores containing much pyrites
may be conveniently roasted in pyrites burners, so that the
sulphur may be recovered as sulphuric acid, whilst lead mattes
and similar smelting products may be treated in kilns with the
same object. The smelting is effected in low blast furnaces
(20 to 26 ft. high), which are always now of the **Pitz and
Rachette** type. The Pitz furnaces are of circular cross-section,
with from four to eight tuyeres. The Rachette furnaces are oval
or rectangular in cross-section. In the shorter or end walls of
the hearth there may be only one tuyere, or perhaps none at
all, whilst in each side wall there may be as many as six. In
such furnaces as have fore-hearths the smelting products are
run out into the hearths which are placed at either end; whilst
those furnaces in which the metal collects in the hearth are
usually provided with the Arents [siphon] tap, together with
one or two slag-notches. In modern American Rachette furnaces
the walls of the boshes and the upper part of the hearth are

built of hollow iron blocks, through which water is circulated whilst the furnace is in blast, in order to keep them cool.

3. The Precipitation Process.—Principles of the Process.—This process is based on the following reaction :—

$$PbS + Fe = FeS + Pb.$$
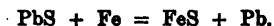
Owing to the tendency of sulphide of iron to form double sulphides a considerable quantity of lead sulphide is used up in the formation of a lead matte ($PbS . nFeS$). This fact must be kept in mind in calculating the charge, especially as the production of this matte is no drawback to the process, for the product is well adapted to use in the manufacture of sulphuric acid, and hence affords a ready means of recovering the sulphur of the lead ore. The matte is calcined in kilns, and the calcined charge, which consists mainly of the oxides of lead and iron, may be used again in a future blast-furnace charge, the iron oxide that it contains serving partly as a flux for silica in the raw ore, and partly as a source of the metallic iron required for the decomposition of another charge of lead sulphide. The iron in the charge is very rarely, if ever, introduced in the metallic state, but is generally used in the form of oxides (such as calcined matte or pyrites, or red or brown hæmatite), or of basic iron-bearing slags (tap or mill cinder) from which the necessary iron is obtained by reduction during the smelting process. The blast furnaces of Pitz or Rachette type are used for this process.

4. Refining of Lead.—Principles of the Process.—In the above-described process, the lead is never obtained pure, but always alloyed with almost all the other metals present in the ores used. Apart from the fact that the useful properties of the metallic lead are seriously affected by these other metals, it is, of course, necessary to recover the precious metal (see Chapter on *Silver*). Of the other metals that may be present in the lead, copper is the most easily separated, inasmuch as it is less fusible than lead, and floats to the surface of the bath when the work-lead is melted at a low temperature. Together with a little lead, the copper is removed by skimming, and then, after liquation (if necessary) from the silver-lead that is mixed with it, it is worked up into copper matte.

Iron, nickel, cobalt, and zinc are removed as oxides by passing superheated water vapour into the melted alloy at a red heat. Arsenic and antimony (the latter metal often being present in considerable proportions) are separated by melting under oxidising conditions, such as are adapted to cupellation for gold and silver. The first litharge, or skimmings, obtained consists mainly of antimonate, with a little arsenate, of lead, and on reducing this a hard lead is obtained containing 15 to 23 per cent. of antimony. Antimony is separated by means of the steam blast from lead that has already been desilverised ; it is

thus removed after the zinc has been oxidised, not by the agency of the combined oxygen of the steam, but by the atmospheric oxygen which is mechanically introduced by the blast.

The separation of bismuth and lead has always been a very tedious process. In the cupellation of the lead, shortly before the "brightening" of the charge, a litharge slag is obtained containing up to 2 per cent. of bismuth. Again, in the refining of the silver, and in the treatment of lead-bearing iron ores, products are yielded which always contain a more or less notable proportion of bismuth. The bismuth is concentrated in these products by repeated smelting and oxidation, a costly operation, which yields a series of oxides containing bismuth in various proportions up to 30 per cent. The richest oxides are then treated in the wet way. Recent experiments made by the author, however, show that the separation of lead and bismuth is very easily effected by electrolysis.

ELECTROLYTIC TREATMENT.

1. Solution by Chemical Agency and Electrolytic Separation of the Lead.—Becquerel's Process.—The treatment of silver-lead ores in the wet way, to which recourse was had in those districts where fuel was expensive, led Becquerel in 1835-1840 to propose the use of the electric current, both to hasten the reactions of the process and better to utilise the precipitating agent.

The electro-chemical treatment of lead ore consists, according to his paper[*] read before the French Academy of Science in 1854, in "so preparing the minerals that the compounds of silver and lead which are obtained from them (when operating on galena) shall be soluble in a saturated solution of common salt; these compounds are the chloride of silver and the sulphate of lead. After the solution has been made, it is allowed to become clear, and is then placed in wooden receptacles, where the decomposition of the metallic salts is effected with the aid of couples of sheet-zinc and either iron, or copper, or masses of well-burnt carbon; couples of lead and the same electro-negative elements may be used instead of the above. The plates of zinc or of lead are enclosed in sail-cloth bags, filled with a saturated solution of salt, and immersed in the metallic solution; the other plates are placed in the latter liquid, and communication is made between the two sets of plates by metal bars. When zinc plates are employed the plates opposing them receive an electro-chemical deposit in the form of very fine particles, consisting of all the metals that are readily reduced, such as silver, copper, and lead; but when leaden plates are used the deposit consists of silver,

[*] *Comptes Rendus*, 1854, vol. xxxviii., p. 109.

which is more or less pure according to the proportion of lead in the solution.

" In place of sail-cloth bags it is preferable to use either boxes made of wood, several millimetres in thickness (which has first been subjected to the action of steam in order to extract any soluble matter), or vessels of half-burned clay, filled as full as possible with pieces of amalgamated zinc and mercury. In this way the action is made more regular, and the quantity of zinc deposited is in atomic proportion to that of the metal deposited.

" By varying the components of the voltaic couple each of the metals present in the saline solution may be separated successively.

" The experiments, of which the results are recorded in my work, were made with quantities of mineral varying from 100 grammes up to 1000 kgms. The quantity of silver recovered in twenty-four hours ranged from a few decigrammes up to 1 or 2 kgms., so that it has been possible to estimate both the advantages and the disadvantages of the electro-metallurgical method of treating the minerals of silver, lead, and copper, but particularly of the former two, of which the preparation is more troublesome.

" Usually the treatment was completed in twenty-four hours, but by operating with the aid of an independent couple, of which the temperature is raised by means of steam, it may be effected in three-quarters of that time. It will be understood that this couple is joined up in voltaic circuit with the other apparatus, which is then provided only with sheets of lead, of which one set is made the electro-positive and the other the electro-negative elements of the pole ; and also that the lead acts directly upon the silver chloride and decomposes it. The two opposing currents which result from this action do not appear to be injurious to the effect of the independent couple. In this manner there is obtained a combination of the advantages of a direct precipitation of silver by means of lead, with those which follow from the electro-chemical action of the independent couple, that transforms each apparatus at the ordinary temperature into a voltaic couple.

" When lead plates are used there is nothing left in the saline solution after a few operations excepting chloride and sulphate of lead, which may be decomposed with the aid of lime."

A later account* contains the statement that 20 tons of ore from Mexico, Peru, Chili, Siberia, Freiberg, Markirch, and various places in France, had been successfully treated in Paris. The *Traité d'Électricité et de Magnétisme*, published by the same author in 1855, contained a very interesting account of a so-called electro-chemical works, in which about 1 ton of ore could be treated at once. The process has never extended, however, beyond the experimental stage.

* *Dingler's Polytechnisches Journ.*, 1869, vol. cxcii., p. 471.

Lyte's Process.—In a more recent process, patented by Lyte,[*] the lead is first converted into chloride, and this is then electrolysed in the molten condition; but it is doubtful whether the process will ever be applicable to actual practice. Crude lead is fused, and is oxidised by a blast of air in a converter; the oxide is then stirred with hydrochloric acid in stoneware vessels until it is completely converted into chloride. At the same time the chlorides of other metals (*e.g.*, of silver) are extracted from the mass of lead chloride by the application of strong hydrochloric acid or of brine. The washed and dried lead chloride is then finally electrolysed in a vessel, the suitability of which is very doubtful. It would almost seem that the action of fused lead chloride upon the material of which the vessel was composed, and the electrical properties of the latter were not known to the inventor at the time that his numerous patent specifications were drawn up. The above account, combined with the references[†] appended, may therefore suffice for this process.

2. Electrolysis of Solutions of Lead Salts with Anodes Composed of Lead Ore.—Concerning this process there is little to be said. A few methods have been devised, of which that of Blas and Miest has already been described in the Chapter on *Zinc* (see p. 286). Enough has already been written in the Chapter on *Copper* as to the treatment of anodes composed of ore compressed or cast into shape.

3. Electrolytic Refining of Lead by the Electrolysis of Dissolved or Fused Lead Compounds with Crude Lead Anodes.—The Keith Process.—Much has been written in the chemical and metallurgical journals concerning the Keith process; and it is reported by some writers to be still in operation in the United States. The attention which the accounts of this process have attracted renders a description of the system necessary, and the following is taken from the *Engineering and Mining Journal*, which was the first to publish a detailed account of the process and plant.

Fig. 160 shows a cross-section, Fig. 161 a longitudinal section, and Fig. 162 a plan of an installation, which was arranged on the basis of a turnover of 10 tons of lead. Figs. 163 and 164 are side and end views of a single tank, the lettering indicating the same parts in each. The former is partly in elevation, partly in section.

The work-lead is melted at the lowest possible temperature in the kettles, *a*, *a*, and thence flows direct into plate moulds. The cast plates, *b*, *b*, are 400 mm. × 1200 mm. × 3 mm. thick [1 ft. 6 in. × 4 ft. × ⅛ in.], and are fastened to metal bars, *c*, *c*, by suitable clamps, *d*, *d*, and with the aid of the rack, *e*, *e*, are enclosed in close fitting bags of coarse muslin.

[*] German Patents 72,804, 74,530, 77,907, and 78,896. English Patents 7264, April 8, and 7594, April 13, 1893. U.S.A. Patent 510,276.
[†] *Cf.* Nernst and Borchers, *Jahrbuch der Elektrochemie* for 1894.

The decomposition vessels are made of boiler-plate or of wood; they measure about $3 \times 1.5 \times 1.5$ metres [$10 \times 5 \times 5$ ft.], and are charged with a solution of lead acetate or chloride.   The cathodes
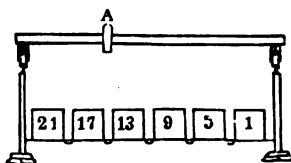
Fig. 160.—Keith's plant.   Cross-section.
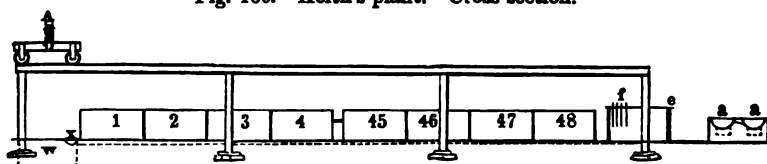
Fig. 161.—Keith's plant.   Longitudinal section.
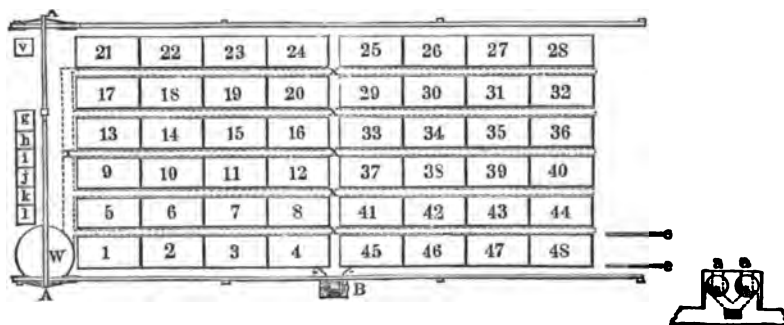
Fig. 162.—Keith's plant.   Plan.
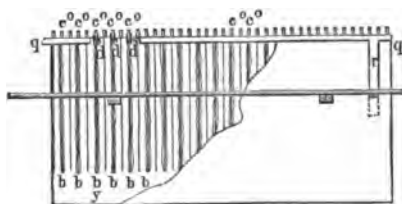
Fig. 163.—Keith's lead-refining vat.   Half section, half elevation.
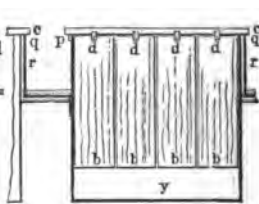
Fig. 164.—Keith's lead-refining vat.   Cross-section, showing anodes.

are thin metal plates which are supported by metal rods, *o*, resting on copper strips, *p*, placed along the upper edge of one long side of each vat.   Along the rim of the other long side is a

second copper bar, q, which is insulated from o and p, as well as from the vat itself; this serves to convey the current to the work-lead anodes which are suspended in bags as above described. The anodes are transported from the racks, e, by the travelling crane, A, and are suspended between the cathodes, in contact with q, and insulated from p and from the walls of the vessel. The baths are arranged in groups of four, all the vats in each group (e.g., 1, 2, 3, and 4, or 5, 6, 7, and 8) being in parallel circuits, whilst the twelve groups of four cells each are coupled in series. The connections between successive groups are made by the conducting rod, r, as shown in Fig. 164. The lead which is deposited upon the cathodes is crystalline in form, and separates continually from the plates, so that a free space, y, is left beneath them to allow for its accumulation.

The method of cleansing and re-charging the vats is usually as follows :—The crane brings up the cathodes to the bath, and meanwhile the solution is run out through x to the reservoir, w, whence it may be pumped again to any required vat. The anode bags suspended from their supporting rods are carried to the reservoir, and the residual solid matter from the plates is washed and returned to the melting pot. The slimes suspended in the wash-water are allowed to deposit, the water is drawn off, and the residue is filtered through the filters g, h, i, j, k, l. These slimes contain antimony, arsenic, silver, gold, copper, and iron, and may be treated by any suitable process.

As soon as the solution has run off, the lead which has fallen from the cathodes is shovelled into suitable moulds, and there pressed into hard cakes. The solution is then pumped once more into the empty tank, the cathodes from the next tank are suspended in it, and fresh anodes, enclosed in bags as usual, are placed in position; the adjoining vessel is then treated in the same way.

In each group of baths there should thus be precipitated 31·1 kgs. [68½ lbs.] of lead per hour, so that the whole installation of twelve groups may be expected to yield about 9000 kgs. [9 tons] of lead in 24 hours. The generator will consume about 12 H.P. for this purpose.

An analysis of these numbers gives the following results :— For the deposition of 68½ lbs. of lead per hour, a current of about 8000 ampères will be necessary. The E.M.F. required is not stated, and a determination of the fall of potential between each pair of plates under the conditions indicated in the above sketch was therefore made by the author. As shown in Fig. 163, Keith hangs four anode plates, 0·4 metre wide and 1·2 metre long on each conducting bar, and 20 of these bars in each bath. The four baths coupled in parallel have therefore a total anode surface of 384 sq. metres [4140 sq. ft.], and the current density is thus found to be 20 amperes per sq. in. [1·86 amp. per sq. ft.].

Under these conditions it was not found possible to use less than 0·4 to 0·5 volt when solution of lead acetate or chloride was employed. But, even if one were to assume that Keith had been able to obtain the desired current-density with an electrical pressure of 0·25 volt in each bath, such as is possible, for example, in the electrolysis of copper solutions with crude copper anodes, the dynamo must have been giving out 12 × 0·25 × 8000 volt amperes [watts] in order to drive a current of 8000 amperes through the twelve groups of baths. This would correspond to *a consumption of about 40 H.P.* Keith, however, speaks of the use of 12 H.P. only; and on the strength of this statement, an estimate of cost, of an unattainably favourable character, has been presented by various technical journals and handbooks. They state commonly that 10 tons of lead may be refined in twenty-four hours with an expenditure of only 12 H.P., and from this it is reckoned that 148 lbs. of coal is necessary to effect the refining of 1 ton of lead, on the basis of 3·9 lbs. of coal being consumed per H.P. hour. From the data given above, it will be seen that from 4 to 5 cwts. of coal per ton of lead would probably be a more correct estimate.

In the above criticism of the Keith process, it has so far been assumed that all the remaining claims of the inventor are sound. Unfortunately, however, these appear, at least in part, to stand upon a somewhat unstable foundation. The use of lead chloride solutions, for example, is quite out of the question. Whether the electrolyte be neutral or acid, there is always a tendency to form peroxide of lead at the anode, even with so low a current density as 20 amperes per sq. metre [1·86 amp. per sq. ft.], especially when the surface of the anode plate begins to grow rough. The E.M.F. necessary under these conditions is higher than would be compatible with the cost permissible in working a refinery process of this description. The author, at least, has not been able to carry on a continuous electrolysis with a lower difference of potential than 1 volt.

Use of Organic Depolarising Agents.—The expenditure of power would not be excessive if lead acetate could be economically employed, and there would be nothing against the use of this electrolyte, if Keith's assertion were correct that the acetic acid suffers no alteration in the process. But this is not so, for the depolarising (and therefore power-economising) influence of all organic electrolytes is traceable to the prevention of lead peroxide deposits upon the anode; and this must always be at the expense of the organic substance itself, which becomes slowly, but surely, oxidised. The products of the oxidation of acetic acid are carbonic acid and water, which have no intrinsic value. In order to prevent false conceptions as to the actual course of electrolysis in this case, it should be stated that the chemical reactions are not such that lead peroxide is formed at the anode,

and that this is reduced by a portion of the organic acid to oxide, which then dissolves in the excess of acid and becomes finally reduced to metallic lead at the cathode. On the contrary, under normal electrolysis, the phenomena are identical with those observed in the electrolysis of other metals of which no peroxides are known, and of which the peroxides are only formed with difficulty. The metal dissolved into the electrolyte at the anode is again separated as such at the cathode, and the impurities present in the crude metal are left undissolved at the anode. Unfortunately, this order of things cannot be always maintained in practice. The impurities present in the crude metal, either as such or in the form of oxide, are for the most part very bad conductors of electricity ; and, as they do not become detached from the anodes as rapidly as could be wished for the smooth working of the process, they tend to form an insulating coating over a large portion of the anode surface. The natural consequence of this is that the current passes mainly through those parts of the plate which remain freely exposed, and so the current density becomes greatly increased, and locally the chemical action of the current far exceeds the limits that are ordinarily imposed. Although it is desirable to select an electrolyte, which in consequence of its oxidisability checks both the separation of lead peroxide and the corresponding increase in the E.M.F. required, yet it must not be forgotten that while these secondary reactions are accomplished, the absorption of power does not come to an end. Indeed, such absorption of power in the production of carbonic acid and water from acetic acid in the Keith process is, to say the least, unremunerative.

[The Tommasi Process.—Another acetate process, in which the electrolyte is the double acetate of lead and potassium (or sodium),[*] has been described by Tommasi. An outline sketch of the process will suffice. Other substances are added to the bath with the acetates, but their nature is not disclosed. The anodes are cast from crude argentiferous lead, and two of these are opposed to each copper, or aluminium bronze, cathode, which is in the form of a disc rotating at the rate of from one to two turns per minute. These discs are about 10 ft. in diameter and ¾ in. thick, and are half immersed in the liquid ; at the upper part are scrapers which serve to detach the small spongy crystals of lead deposited during electrolysis. The crystals thus removed fall into channels which convey them to a sieve of wire gauze, where they are drained and washed, the washings being concentrated by evaporation to 20° Baumé (sp. gr. = 1·256), and used again as electrolyte. The lead is then compressed, mixed with 2 to 3 per cent. of charcoal powder and fused. The silver with most of the arsenic and antimony is separated at the anode,

* *Comptes Rendus*, 1896, vol. cxxii., p. 1476. See also *Aluminium and Electrolysis*, 1896, vol. i., p. 61.

and is collected in trays, to be fused subsequently with sodium nitrate and a little borax, by which it is separated from arsenic and antimony. No details of current strength are given. The author estimates the cost of extracting the silver from the work-lead at from 8 to 10 francs per ton when steam power is employed to run the dynamos.—TRANSLATOR.]

Uses of Spongy Lead.—It may, however, so happen that the electrolytically deposited lead shall have properties, which render it particularly suitable for some special purpose, so that the increased cost involved is of no very great importance. As a matter of fact this is the case; for the lead is never obtained from aqueous solutions in a dense coherent form, but always as the so-called lead sponge. Keith recommends that the deposit on the cathodes of his apparatus should be compressed and then fused; but the spongy deposit that is so troublesome to the metallurgist, is found to be invaluable in the preparation of electrical accumulators, and is even, in some places, specially prepared from pure lead for the purpose. For such cases as these, the electrolytes mentioned in the Chapter on *Zinc* might be recommended. There are so many products of tar-distillation for which there is scarcely any market that the employment of the more expensive acetic acid or acetates is quite unnecessary. The mixture of cresols, technically known in commerce as fluid carbolic acid, when mixed gradually with strong sulphuric acid, and digested for some time at a temperature of from 50° to 100° C., is easily converted into cresol-sulphuric acids, which are themselves soluble in water, and are also capable of forming easily soluble salts with lead. Before employing this reagent, care must be taken to precipitate any free sulphuric acid that may be present by the addition of baryta or of barium carbonate. But with a current density of 20 amperes per sq. metre [0·013 amp. per sq. in.], as recommended by Keith, a difference in potential of 0·5 volt has been found to be necessary, and hence, at least, 7·2 electrical H.P. (or nearly 9 I.H.P. in the water, gas, or steam engine) would be needed to produce 1 ton of lead in 24 hours, or in the last-named case over 200 kgs. [4 cwts.] of coal in a very large installation.

Electrolysis of Fused Lead Salts.—If, however, the usual market-lead of commerce is to be produced (which is always sold in the form of solid ingots), the electrolysis of aqueous solutions is not admissible as a process of refining, for the fusion of spongy lead cannot be effected without the formation of much dross, which then requires further treatment. It is, however, only by the treatment of fused salts that an electrolytic refining of lead in the proper sense of the word would be suitable, in order to obtain a directly marketable product. Such a process has already been referred to in connection with the difficulties accompany-ing the treatment of material containing bismuth in the refining

of lead. It is evident at a glance that, in the ordinary method of working with this bismuth alloy, an altogether disproportionate expenditure of labour and fuel must be made for a comparatively insignificant result. Having regard, however, to the heats of formation of lead and bismuth compounds, it would certainly appear probable that, given a suitable apparatus and a moderately fusible electrolyte, the electrolytic method of treatment might not only be possible but might even offer distinct advantages in use, having in view the direct production of valuable and marketable materials, such as bismuth and soft lead. It is an easy problem to find a suitable electrolyte, and the difficulties to be encountered lie solely in the arrangement of the apparatus.

Borchers' Apparatus.—The author has overcome these difficulties by using an apparatus of the form now to be described. Fig. 165 shows a vertical cross-section, Fig. 166 a plan of the empty apparatus as seen from above, and Fig 167 a longitudinal view in half-section, half elevation. The melting vessel consists of three cast-iron parts : a and k are half-cylinders lying horizontally ; a is bounded by a sloping wall on the left, and k by another on the right. Between the two is a hollow iron half-ring, v, which is so formed that it has practically the shape of an inverted T in cross-section. Thus there are produced two semi-circular groove-like channels, which serve to contain an insulating material, and which receive the flanges, f, f, of the two half-cylinders, uniting the whole apparatus into one melting vessel, of which the three principal parts are insulated from one another. The hollow ring, v, is water-cooled with the aid of the pipe, e. The water is allowed to escape by x ordinarily, or by s if its free passage through the apparatus should chance to become hindered. The tubes, r and p, are used both to regulate the level of the fused material in the trough and to remove the reduced metal. The apparatus is heated by means of the flue, h, which surrounds it, and through which heating gases *free from smoke* are passed.

In using the apparatus, water is caused to circulate through the ring before heating is commenced, and great care is taken that this circulation shall not be hindered at any time during the progress of the operation. After heating, lead is introduced through r and p in such quantity that some of the metal enters into each half of the apparatus. A mixture of alkaline chlorides in molecular proportion (KCl + NaCl) is now melted in the vessel, or if a still more fusible mixture be required, an alkaline earth chloride is mixed with the others. If the fusion be effected in the vessel itself, the mixture must be introduced, a little at a time, as it melts ; for large quantities of salt are only melted with the greatest difficulty if introduced in mass. It is, however, best to melt the salts in a separate vessel, and to pour the fused

substance into the electrolytic apparatus after the latter has been
sufficiently pre-heated.   During the operation care must be taken
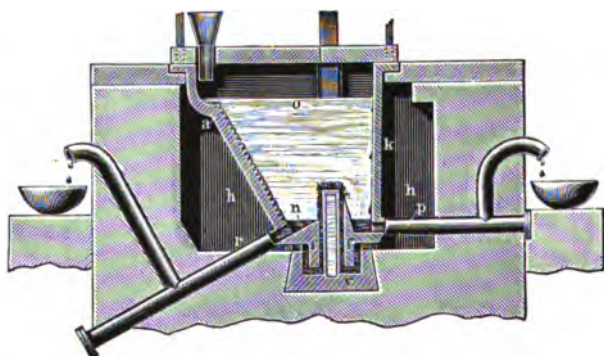
Fig. 165.
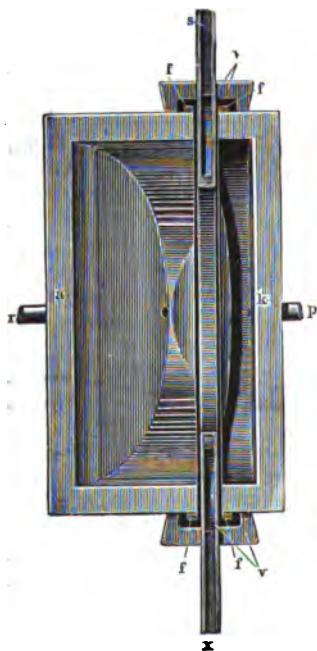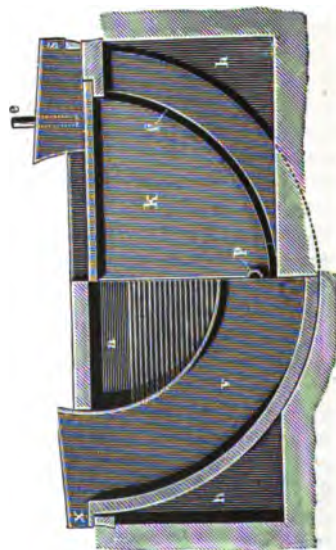
Fig. 166.   Fig. 167.

Borchers' lead-refining plant.

that the salt *does not gain admission to the tubes,* and, to prevent
this, it is advisable to add some lead at intervals, but not so

much that the metal is visible on the bottom. The electrolyte must be kept strongly basic, as, otherwise, the iron (especially in the anode compartment) will be vigorously attacked, and the apparatus will soon become perforated. For this purpose litharge should be added; and this material dissolves more readily in the salt if it be intimately mixed with lead chloride, or converted into oxychloride by treating it with hydrochloric acid. These lead compounds must not be added until the melting pot is nearly full, because metallic iron surfaces cause a separation of lead from it, and this is apt to produce short circuits if it penetrate the insulating material prematurely. Although at the commencement the introduction of the lead compounds at too early a stage may be a disadvantage, yet when once the iron surfaces in the neighbourhood of the cooling ring have become coated over with a non-reducible and insulating crust of solidified salt, it is necessary to add them throughout the whole course of subsequent electrolysis. The potassium chloride, as it becomes vaporised, is therefore best replaced by lead oxychloride. There is no fear of the apparatus failing at the joints, because, even if melted matter should penetrate the insulating material (clay free from carbon, sand, marl, &c.), it would there solidify, and thus tend even to stop the leak. The author has adopted the same principle of making secure joints in other apparatus.*

After the addition of the lead salts, the raw lead must be charged through the hopper, and the current must be switched on. In this way the lead which trickles over the terrace-troughs of the anode wall, *a*, is for the most part dissolved, while a corresponding quantity of metallic lead is deposited by the current or the cathode wall, *k*. When the current density does not exceed 1000 amperes per sq. metre [0·645 amp. per sq. in.] scarcely a trace of bismuth dissolves. But if there be very little of this latter element initially present, a current density of 6000 amperes per sq. metre [3·87 amp. per sq. in.] of anode surface may even be employed without danger of solution. As the percentage of bismuth increases, the current density is again reduced. It is advisable not to allow the metal that is to be refined to pass too slowly through the apparatus, but rather to renew the surface frequently by passing the metal repeatedly through the same apparatus, or through several in succession, until it is sufficiently enriched. By keeping the current within the limits named above it is possible to obtain, without loss of metal, not only a very pure soft lead, but a crude bismuth containing from 90 to 95 per cent. of that metal. The small proportion of lead in this bismuth is readily removed by well-known and simple smelting processes. The lead separated during electrolysis escapes through the pipe, *p*. The external orifices of the tubes, *r* and *p*, must be so placed that the level of the fused salt shall stand at the line, *o*, and that of the melted lead at *n*.

* Compare the sodium apparatus, p. 61.

With the current density recommended above, the E.M.F. required is about 0·5 volt, so that nearly 4·5 kgs. [10 lbs.] of lead should be deposited per H.P. hour.

The apparatus has at present been used only for experiments with 2-H.P. dynamos.

Applications of Lead.—On account of its physical properties lead is largely used for casting, for bullets, for safety fuses in electrical installations, and in making pipe joints. By reason of the readiness with which it dissolves other metals, it is used in the extraction and refining of the noble metals, and it also forms a series of useful alloys. Thanks to the chemical properties of the metal, lead is largely employed for water, acid, and gas-pipes, for the production and lining of chemical apparatus, and for the manufacture of electrical accumulators.

CHAPTER VIII.

BISMUTH.

Properties and Occurrence of Bismuth. — Bismuth (Bi; atomic weight = 208; specific gravity = 9·74 to 9·8) is a bright pinkish-grey metal with a brilliant lustre and a large foliated crystalline structure. At the ordinary temperature it is so brittle that it may be readily broken down and pulverised. In spite of its low thermal conductance it is a relatively good conductor of electricity. Bismuth melts at 264° to 270° C.; its boiling point has not been accurately determined, but lies between 1100° and 1600° C. In the fused condition it is an excellent solvent for many metals, and is itself readily dissolved by these and other metals; among the latter are the noble metals, and (chiefly) in addition to these, lead, tin, zinc, cadmium, copper, nickel, the alkali and alkaline earth metals. The alloys of bismuth with the first-named metals are distinguished by very low melting points whilst those with copper and nickel (bismuth bronzes) are exceedingly hard.

At the normal temperature, bismuth is capable of withstanding for a long time atmospheric influences, oxygen, or weak acids; but at higher temperatures it oxidises comparatively readily in air, but not quite so easily as lead. Steam has but little action on the metal even when it is red-hot. Among the ordinary acids, hydrochloric acid attacks bismuth only in the presence of oxidising agents, slowly even in the presence of air; nitric acid acts more rapidly if it be not too dilute; hot concentrated sulphuric acid dissolves bismuth, with evolution of sulphur dioxide, and forms the sulphate. It forms several oxidation products;

but only the oxide, Bi_2O_3, and the compounds derived from it possess any interest technically. The neutral salts are converted very easily into the difficultly soluble or almost insoluble basic salts.

Bismuth is precipitated from the solutions of its salts by a large number of other metals, such as zinc, manganese, iron, nickel, cadmium, tin, copper, and lead, as well as by the alkali and alkaline earth metals. It is worthy of note in connection with the refining of bismuth that lead can separate this metal completely even from fused oxides and basic salts.

Bismuth occurs comparatively rarely in nature, whether in the metallic state or in the form of an earthy ore. Native bismuth; the oxide, Bi_2O_3, as bismuth ochre, and the sulphide; Bi_2S_3, as bismuthine; occur sufficiently often to provide material for a small metallurgical work. It is also found as sulphide in various sulphide and arsenical ores of cobalt, nickel, copper, lead, and silver.

Extraction of Bismuth.—Mention can here be made only of the direct method of extracting bismuth from oxide and sulphide ores and products. The processes employed in the treatment of ores in which another metal predominates will be described in the chapter relating to the element in question.

Eliquation.—This method is only available for metallic ores or products, and is but rarely practised now, because the residue retains so much metal that it must of necessity be re-smelted.

The Reduction Process.—Oxidised ores and products are smelted upon the hearth of a small reverberatory furnace, or in crucibles, in admixture with soda, limestone, slags from previous operations, and carbon. When basic bismuth salts are to be treated (the oxychloride especially occurs now and again) they must not be smelted until they have been thoroughly mixed with burnt or slaked lime. This may be effected by means of a mill, or by stirring the ore with milk of lime and subsequently drying, or by other suitable means, so that the chlorine, or any other substance present that is capable of forming volatile compounds and causing loss of bismuth, may be combined with lime. The use of soda in the charge should not be too sparing, because it gives to the slag an additional fluidity which is necessary owing to the comparative readiness of bismuth to volatilise. The ingredients of the charge should be so proportioned that the slag consists of a silicate intermediate in composition between a bi- and a mono-silicate. The bismuth so obtained is not pure but nearly always contains some lead, arsenic, and antimony, frequently with other metals such as copper in addition.

The Precipitation Process.—Just as in the smelting of lead, sulphide, and arsenical ores may be treated by fusion with iron. In this case a slightly basic slag is used, and scrap iron is added to the charge, the fluxes being the same in kind as in the last

case, but altered somewhat in proportion. The copper in the ore passes into matte as sulphide. Cobalt and nickel are usually accompanied by arsenic, and in this case a speise is formed ; but in spite of this a little arsenic always finds its way into the bismuth. Lead and antimony also enter the latter. It is therefore necessary, in this instance as in the last, to refine the metallic product.

Chemical Solution and Precipitation.—This forms the so-called **wet method of extracting bismuth,** and can be used only for the enrichment or chemical preparation of ores containing bismuth—or of metallurgical products rich in lead ; because it affords an oxidised compound of bismuth, which has then to be smelted by the reduction process. It has been explained in the Chapter on *Lead* that in the smelting of lead or silver ores containing bismuth there is first obtained an alloy of the metals that retains its bismuth until the last stages of the silver-extraction process. The litharge containing about 20 per cent. of bismuth resulting from the enrichment above described, as well as the hearth of the cupellation furnace, and the slags from the Rössler refining process, are all, as a rule, treated by the wet method. This consists in treating the finely-crushed product with moderately strong hydrochloric acid, in order to bring the bismuth into solution as chloride whilst leaving the bulk of the lead in the insoluble condition. On running this solution into a large volume of hot water, the bismuth is deposited as a basic chloride, whilst the lead remains in solution. After washing the precipitate, which may be again dissolved and treated in the same way, it should be digested with milk of lime, washed, filtered, and dried; and the resulting product should be treated by the reduction process.

The Refining Process.—For the refining of crude bismuth numerous processes have been devised, which may have been well enough suited to some special sample of metal, but which have been described without this qualification in the journals, and the descriptions have thence been copied into the metallurgical text-books as general methods applicable in all cases.

The principal impurities in crude bismuth are lead, arsenic, and antimony ; and the refining of the metal is conducted according as one or other of them preponderates. If the selection of the method be correct the loss of bismuth should be very small, although the text-books may state otherwise.

If any notable proportion (*e.g.,* more than a fraction of one per cent.) of lead be present, it would be undesirable to fuse the metal with caustic alkali and nitre, as is sometimes recommended, because plumbic salts would be formed, and would act as carriers of oxygen, thus giving rise to a very considerable loss of bismuth. Lead is easily removed by melting in an iron pot first a mixture of potassium and sodium chlorides, to which

some caustic soda has been added, and then the metal to be refined, a quantity of bismuth oxychloride corresponding to that of the lead to be removed being introduced simultaneously with the crude bismuth. The mixture is stirred for from two to three hours, according to the amount of lead present. As soon as a test portion of the bismuth is found to solidify with a largely foliated crystalline structure the fire is drawn, an iron hook is inserted in the pot, and the whole is allowed to cool. The slag is removed by solution in water after cooling, and the metal is then lifted by the inserted hook and broken up.

If the bismuth still contain arsenic or antimony, or if these metals should be present without lead in the original sample, the bismuth is fused with caustic soda and nitre. Over-heating must be carefully avoided, but otherwise the method corresponds with that last described. The metal is only smelted with sulphides (soda and sulphur) when a very large proportion of antimony is present. The remaining impurities, which are usually few, are removed by one of the other methods of treatment.

The essential features of all these smelting processes are :— An easily fusible mixture, as low a temperature as possible, and a thorough stirring of the charge. No universal recipe can be given to guide the proportionment of slag to metal, although it might seem possible to find one from text-books. The proportions of the impurities present vary almost every time, and the addition of fluxes and refining media must be made to correspond.

Electrolytic Methods.—The raw materials already described afford but scant opportunity for electrolytic treatment. The almost solitary instance of lead and bismuth separation has been given under *Lead*, since in that case it is the lead and not the bismuth which is really electrolysed. As was explained in the Chapter named, it is not advisable to enrich the bismuth beyond a 95 per cent. alloy by electrolytic solution of lead ; otherwise the current density towards the end of the electrolysis would have to be so far reduced that the relative expenditure in maintaining the whole mass in the fused condition would be more costly than the application of a purely chemical refining process. The enriched product, therefore, at the limit named, should be refined by the method recommended in the last paragraph.

The Applications of Bismuth.—The use of bismuth is practically restricted to the production of easily fusible (Wood's, Rose's, Lipowitz', &c.) and to hard (bismuth bronze) alloys, and to some compounds, such as bismuth subnitrate and oxychloride, which are used for pharmaceutical and cosmetic preparations.

CHAPTER IX.

ANTIMONY.

Properties of the Metal.—Antimony (Sb; atomic weight = 120; specific gravity = 6·7), the most metal-like of the non-metals, is white, and has a good metallic lustre. The fractured surfaces of pure antimony show a largely foliated crystalline structure, whilst on the outer surface of the so-called "antimony regulus," a star-shaped crystalline marking is observed. Antimony is very brittle, and may be easily crushed to powder. It fuses at about 440° C., and boils at a temperature between 1100° and 1400° C. Antimony is the most electro-negative element in the thermo-electric series, and is therefore a valuable material for the construction of thermopiles.

Oxygen and water alike are almost without action on antimony at the normal temperature. Among the acids, hydrochloric acid has a slight solvent action; nitric acid oxidises it to the pentoxide; strong sulphuric acid first oxidises the metal, and the resulting oxide then forms a sulphate with the excess of acid. Chlorine reacts directly with metallic antimony, and the reaction may be utilised in the production of anhydrous chloride of antimony. With most metals, antimony forms chemical compounds (speise and antimony alloys), which exhibit a certain hardness and brittleness, as well as a great power of resistance to chemical influence.

Antimony forms two simple oxides of technical importance, the trioxide, Sb_2O_3, and pentoxide, Sb_2O_5, of which the former is chiefly basic, and the latter is more acid in character; but each is capable of acting as an acid towards the alkalies and other strongly basic substances. Among those salts in which antimony is the base, almost the only compounds for which there is any practical application are the haloid salts, $SbCl_3$, SbF_3, $SbCl_5$, some double compounds of these with alkali metal salts, and tartar emetic. Of the salts which contain the antimony in the acid radical, the compounds of the trioxide, or antimonious oxide, are known as the antimonites, whilst those derived from the pentoxide, or antimonic oxide, are designated antimonates. So also the corresponding sulphides, Sb_2S_3 and Sb_2S_5, form thio-salts, similar in constitution to the oxide compounds just described, and known as thio-antimonites and thio-antimonates. All these

salts are for the most part produced only as intermediate products in the preparation of antimony compounds or of metallic antimony.

Occurrence of Antimony in Nature.—Of the antimony compounds occurring in nature, these chiefly used in smelting are the sulphide, Sb_2S_3, known as antimony-glance, grey antimony, stibnite, or antimonite, and the oxide, Sb_2O_3 (valentinite and senarmontite). According to the nature of the ore, the one or the other of the following alternative processes is used in the smelting of antimony.

The Precipitation Process.—This method of reduction is based on the following reaction, $Sb_2S_3 + 3Fe = Sb_2 + 3FeS$. The richer sulphide ores, containing 50 to 90 per cent. of Sb_2S_3, are smelted direct, the poorer ores are first liquated to concentrate the sulphide, as *antimonium crudum;* the sulphide is then melted in crucibles or reverberatory furnaces along with scrap iron and basic additions. For the latter, a mixture of sodium sulphate and carbon is used, which yields sodium sulphide on heating. The antimony thus obtained contains too many impurities (iron, &c.) to be used directly, and is therefore submitted to a repeated refining operation, as will be explained in treating of the purification of antimony. In conducting this operation, either a reverberatory furnace may be used, or plumbago crucibles, of which any number, up to 40, are commonly placed together in a heating chamber. The crucible smelting process is described fully in the under-mentioned journals.[*] For the reverberatory furnace process, the greatest difficulty is the production of a solid hearth, since melted antimony finds its way even into the finest cracks. This difficulty has been overcome in a furnace constructed by the author, and shortly to be described.

The Reduction or Roasting and Reduction Process— Oxidised ores can be reduced directly; sulphide ores only after an oxidising roast. The roasting may be effected according to either of two principles, namely : — by employing as low a temperature as possible with an insufficient air supply, in order to produce the volatile antimonious oxide, or by using a higher temperature and an excess of air, in order to convert the sulphide as far as possible directly into antimonious antimonate. The former method is very difficult to apply, and is only adopted, as a rule, when antimonious oxide is to be prepared commercially. Any muffle furnace which permits of a thorough control over the temperature may be used. The roasted ore obtained by either process is smelted in a reverberatory furnace, with the addition of slags from a previous operation, together with Glauber's salt [sodium sulphate], and, if necessary, soda. As to

[*] *Journ. Soc. Chem. Ind.*, 1892 (vol. xi.), p. 16. *Zeitschrift für angewandte Chemie*, 1892, p. 146.

the construction of the reverberatory furnace, the remarks made
in the last paragraph are equally applicable here.

The slag from the lead-softening furnace, consisting of lead
oxide and antimonate, may be worked up by this process. This
slag may also be treated in low blast furnaces, but of course it
then affords a "hard lead," consisting of an alloy of lead anti-
monide, with varying proportions of lead, instead of anti-
mony.

Electrolytic Processes. — **Methods available.** — The direct
electrolytic treatment of antimony glance is out of the question.
If, therefore, it be desired to extract antimony from its ores by an
electrical process, it is necessary first to bring the antimony into
solution by ordinary means, and then to precipitate it electro-
lytically. The electrolytic refining of antimony has not been
successful, because either the electrolytes hitherto available were
too costly, or the metal was obtained in an unsatisfactory
condition.

Of the oldest processes on record for the electrolytic deposition
of antimony, that recommended by Gore [*] and by Böttcher,[†] in
which a solution of the trichloride was used, cannot be employed,
by reason of the explosive properties of the deposit. The first
practical method was that recommended by Luckow,[‡] Classen
and Ludwig,[§] for analytical purposes; and in this the thio-salts
of antimony were used. The author, in 1885-1886, endeavoured
by exhaustive experiments to determine the conditions favourable,
not only to the deposition of the antimony, but to the recovery
in useful form of the sulphur that had been combined with the
antimony as well as that from the solvent itself.

Borchers' Experiments on Antimony Refining. — The
results of two experiments conducted on a large scale may be
given by way of illustration :—

1. 9·620 kgm. of Schlippe's salt [sodium thio-antimonate] was
dissolved in sufficient water to give a solution of 10° to 12°
Baumé. Sufficient caustic soda solution was then added to give
80 pts. NaOH to 962 pts. $Na_3SbS_4 + 9H_2O$, so that the liquid
then contained the two substances in proportion corresponding
to the formula $2(Na_3SbS_4 + 9H_2O) + 2NaOH$. A little common
salt was added by way of improving the conductance, and the
solution was then submitted to electrolysis. The appropriation
of the elements before and after the experiment is shown in the
following table :—

* *Chemical Gazette*, 1858, p. 59, and *Chemical News*, 1863, vol. viii.,
p. 201.
† *Journal für praktische Chemie*, vol. lxxiii., p. 484.
‡ *Zeitschrift für analytische Chemie*, 1890, vol. xix., p. 14.
§ *Berichte der deutschen chemischen Gesellschaft*, 1885, vol. xviii., p. 1104.
A. Classen, *Quantitative Analyse durch Elektrolyse*, 3rd. ed., Berlin, 1892.

	Antimony.	Sodium.	Sulphur.	Oxygen.
Before Electrolysis— In form of salts, &c., . .	Kgrm. 2·440	Kgrm. 1·840	Kgrm. 2·560	Kgrm. 0·320

After Electrolysis—
  In metallic form, . . .
  In solution—
   2·410 kgm. NaSH, . .
   1·202 ,, Na$_2$S$_2$, . .
   1·491 ,, Na$_2$S$_2$O$_3$+5H$_2$O,
	2·437
	
	...
	...
	...
		...
		
		0·990
		0·503
		0·275
			...
			
			1·377
			0·699
			0·384
				...
				
				...
				...
				0·288

	2·437	1·768	2·460	0·288

The loss of antimony (3 grm.) is here so small that the precipitation may be considered as practically quantitative. The loss of sodium (72 grm.) and sulphur (100 grm.) are explained by the fact that the solution clinging to the antimony after the powder had been removed was not added to the rest of the liquid, for reasons which will be explained hereafter in describing the method of treating the deposited metal. The ratio 72 : 100 agrees sufficiently well with 1768 : 2460 to confirm the above statement. The quantity of oxygen actually obtained must also have been larger than that shown, and in the same proportion; it should, therefore, be 300 instead of 288 grm.

2. In the next experiment a solution was electrolysed, which contained 3·400 kgrm. of Sb$_2$S$_3$ and 7·200 kgrm. of Na$_2$S + 9H$_2$O, corresponding to the formula Sb$_2$S$_3$ + 3Na$_2$S. The solution was made up to about the same specific gravity as that of the electrolyte in the previous case, and was also mixed with a small quantity (2 to 3 per cent.) of common salt. Adopting the same system of recording, the results of the experiment are shown in the following table :—

	Antimony.	Sodium.	Sulphur.	Oxygen.
Before Electrolysis— In form of salts, . . .	Kgrm. 2·440	Kgrm. 1·380	Kgrm. 1·920	Kgrm. ...

After Electrolysis—As metal, .
  In solution—
   1·290 kgm. NaSH, . .
   1·200 ,, Na$_2$S$_2$, . .
   1·563 ,, Na$_2$S$_2$O$_3$+5H$_2$O,
	2·435
	
	...
	...
	...
		...
		
		0·530
		0·502
		0·289
			...
			
			0·737
			0·698
			0·403
				...
				
				...
				...
				0·302

	2·435	1·321	1·838	0·302

Here again the deposition of the antimony was practically quantitative. The loss of sodium (59 grm.) and of sulphur (82 grm.) is due, as proved by the proportion existing between them, to the solution adhering to the pulverulent antimony deposit. The ratio of 59 : 82 is sufficiently near to that of 1321 : 1838 for this proportion, and the proportion of oxygen indicated in the table must therefore be increased to 315 grm., to correspond with this.

As shown by the above experiments, it was sought to provide for such a ratio between the sulphur and the sodium taking part in the reaction that for every atom of the one there should be also one atom of the other. Any ratio in which the sulphur present exceeds, or the sodium is less than, this amount leads to an interference with the steady progress of the operation. The opposite case (with more sodium or less sulphur) leads to an increased electrical resistance of the solution, and therefore is also unsatisfactory.

According to the evidence afforded by the products of the reaction it would seem that the antimony sulphide has not taken part alone in the electrolysis; but the presence of the three products, sodium hydrosulphide, disulphide, and thiosulphate, tends to support the idea that they were produced indirectly. In any case, the formation of the sodium hydrosulphide can as little be explained without supposing the intervention of water, as can the presence of thiosulphate without that of oxygen. But if, on the contrary, it be considered that water or sodium hydroxide were electrolysed prior to the deposition of antimony an easy explanation would be offered to account for the formation of the above products. Hence, from these two experiments, it may be considered that by the electrolytic action of a certain quantity of current, 6 atoms of hydrogen and 3 atoms of oxygen were rendered available, and that in the second experiment they produced the following reactions :—

$$\text{I. } 2Na_3SbS_3 + 6H = Sb_2 + 6NaSH.$$
$$\text{II. } 6NaSH + 3O = 3H_2O + 3Na_2S_2.$$
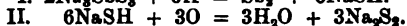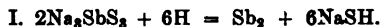
Had these reactions been carried to completion, it would have been impossible to decide whether the equation representing the result of the electrolysis were not simply

$$2Na_3Sb_2S_3 = Sb_2 + 3Na_2S_2$$
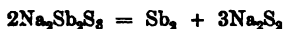
instead of that suggested. But according to the analyses quoted it would appear either that this reaction is only partial, or that, of the above equations I. and II., the latter is not completed owing either to an insufficient circulation of the solution, or to the use of too great a current density, or the like, the result being that a part of the oxygen is used up in converting a portion of the disulphide into thio-sulphate. From equation II.

it may be calculated that 0·174 kgrm. of oxygen would be necessary to the formation of the 1·200 kgrm. of Na$_2$S$_2$ found by analysis to be present in the electrolysed liquid. The total weight of oxygen used for the formation of Na$_2$S$_2$ and Na$_2$S$_2$O$_3$ in experiment 2 is therefore 0·485 grm., which corresponds exactly to the work of three atoms of oxygen liberated per two atoms of antimony during electrolysis.

In the first experiment the reaction is not so apparent because oxygen was present in combination with sodium in the form of hydroxide at the outset. But, accepting the view that the deposition of the antimony is due to the indirect action of the current, the following equation would distinguish the removal of the oxygen initially present from that effected in the main reaction :—

$$2Na_3SbS_4 + 2NaOH + 6H = Sb_2 + 2Na_2S_2 + 4NaHS + 2H_2O.$$
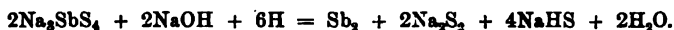
Applying in this case a computation of the oxygen necessary to the formation of the disulphide and thio-sulphate present, similar to that used in connection with the second experiment, it will be seen that 0·475 kgrm. of oxygen should be required. This, again, agrees very well with the separation of three atoms of electrolytic oxygen for two of deposited antimony.

Whether or not this explanation be correct, the experiments clearly show that the thio-antimonate, Na$_3$SbS$_4$, requires no greater expenditure of power than does the thio-antimonite, Na$_3$SbS$_3$, although the antimony in the former case must be regarded as pentavalent (3Na$_2$S + Sb$_2$S$_5$ = 2Na$_3$SbS$_4$), and in the latter case as trivalent (3Na$_2$S + Sb$_2$S$_3$ = 2Na$_3$SbS$_3$). Antimony appears, therefore, to form only trivalent ions in sulphide electrolytes. In full accord with this is the observation that the so-called pentasulphide, precipitated from the purest solutions of antimonates, always yields to carbon bisulphide so much sulphur that the residual matter contains antimony and sulphur in the proportion required by the tri-sulphide. In aqueous solution, as well as in the free condition, there appears, therefore, to be no pentasulphide of antimony.

Conditions Suitable to Electrolytic Refining of Antimony. —It has been affirmed by some that this method must in all cases be too costly. Undoubtedly, it would be so if it were necessary to purchase the sodium sulphide required for the reaction, and if the solution were run to waste after it had been electrolysed. But there are circumstances under which the method might be utilised with advantage, and some of these may here be shortly examined into :—

1. The simplest case would be that in which a cheap source of sodium sulphate was available. In countries, or in industrial centres, in which hydrochloric acid is manufactured as a main product (and not incidentally as in the Leblanc soda process),

sodium sulphite would be a bye-product.   The process would then consist of the following stages : —

(a) Reduction of the sulphate to sodium sulphide by heating with carbon.

(b) Leaching of the product ; in which case the cost of clearing, evaporating, crystallising, packing, and freight of the sodium sulphide would not be included, because the liquors would be utilised in the next stage.

(c) Solution of the antimony ore in the sodium sulphide solution.

(d) Electrolysis of the clear solution, and deposition of antimony.

(e) Fusion of the antimony.

(f) Oxidation of the electrolyte by means of air, and concentration of the resulting thio-sulphate.

Thus, from the raw materials, sodium sulphate, carbon, and antimony ore, there would be produced antimony and sodium thio-sulphate.

2. It is, therefore, evident that hydrochloric acid manufacturers might adopt this process, in order to find a profitable use for the comparatively unsaleable sodium sulphate.   In this instance the raw materials would be sulphuric acid, or the sulphides necessary for its manufacture, common salt, coal, and antimony ore, while the marketable products would be hydrochloric acid, antimony, and sodium thio-sulphate.

3. In districts in which there is no demand for hydrochloric acid, the process might be altered but slighly, thus :—

(a) Manufacture of sulphuric acid from a part of the sulphur recovered at the end of the operation.

(b) Sodium sulphate and hydrochloric acid prepared from sulphuric acid and common salt.

(c) Sodium sulphide prepared from sulphate and coal.

(d) Leaching of the antimony ore.

(e) Electrolysis of the antimonite lye.

(f) Fusion of the antimony.

(g) Recovery of sulphur from the spent electrolyte with the aid of the hydrochloric acid, more than half of the sulphur being thus reconverted into sulphuric acid, and the residue being sent into the market as such, or in the form of sulphuric acid.

In this case the raw materials would be :—Sodium nitrate, air and steam for the sulphuric acid plant, common salt (to the amount of the working loss, the greater part of that used being recovered), coal, and antimony ore.   Whilst the finished products would be antimony and sulphur or sulphuric acid.

Practical Working of the Electrolytic Process.—The following is a short sketch of the conditions that would obtain. in laying down and working an installation of this process. on a large scale, with illustrations of the electrolytic vessels

recommended for the purpose. The sulphuric acid, sulphate, and sulphide manufactures are better dealt with in the hand-books relating to the manufacture of these substances than they could be in the space here available.

The leaching of the ore is effected in the conical iron vessels, a (Figs. 168, 169), the sodium sulphide solution being heated, and at the same time agitated, by means of steam introduced through the steam-pipe, b. As soon as the solution is boiling, the finely-divided ore is sprinkled into it. Any antimony compound may be used that is readily soluble in solutions of sodium sulphide. The presence of sodium hydrosulphide or of polysulphides is not objectionable, provided that the proportion of sulphur to sodium is kept (by the addition of soda) within the limits already prescribed—viz., that in the solution to be electrolysed, *every atom of oxidisable sulphur shall be accompanied by an atom of sodium capable of neutralisation.* On this account the use of sodium sulphide must not be too sparing. For example, the production of an aqueous solution of $Sb_2S_3 + Na_2S + 2NaOH$ is quite possible, but the mixture is so unstable that even during the clearing of the solution, a separation of antimony compounds may take place.

Antimony glance is best suited for treatment, and even very poor ores may be worked advantageously, since antimony trisulphide is readily soluble in extremely dilute solutions of sodium sulphide. There should be present in the solution three molecules of sodium sulphide for each molecule of antimony trisulphide; and after the extraction is complete the concentration should not exceed 12° Baumé (or 9° to 10° if hot). About 3 per cent. of common salt, reckoned on the whole quantity of electrolyte, should then be added. This serves both to assist the clearing of the solution by the separation of dissolved sulphide of iron, and to reduce the electrical resistance of the solution. If the spent electrolyte be ultimately worked up into sodium thio-sulphate, the sodium chloride is separated out again during the final evaporation.

After the requisite quantity of ore has been added to the liquid in the extraction apparatus, the mass is stirred thoroughly by a current of injected steam for an hour or longer according to the degree of fineness to which the ore has been reduced. From time to time air is admitted with the steam, by the operation of a steam-injector, c, on the steam-pipe, b.

When the heating and stirring have been continued sufficiently long, the insoluble portion of the charge is allowed to deposit, and the clear solution is afterwards (after two to three hours) drawn off through the pipe. Since, however, the height of the deposit in the vessel varies in different charges, the bell-shaped siphon arrangement, d, is used to ensure that only the clear liquor is drawn off. This siphon consists of a wide tube,

23
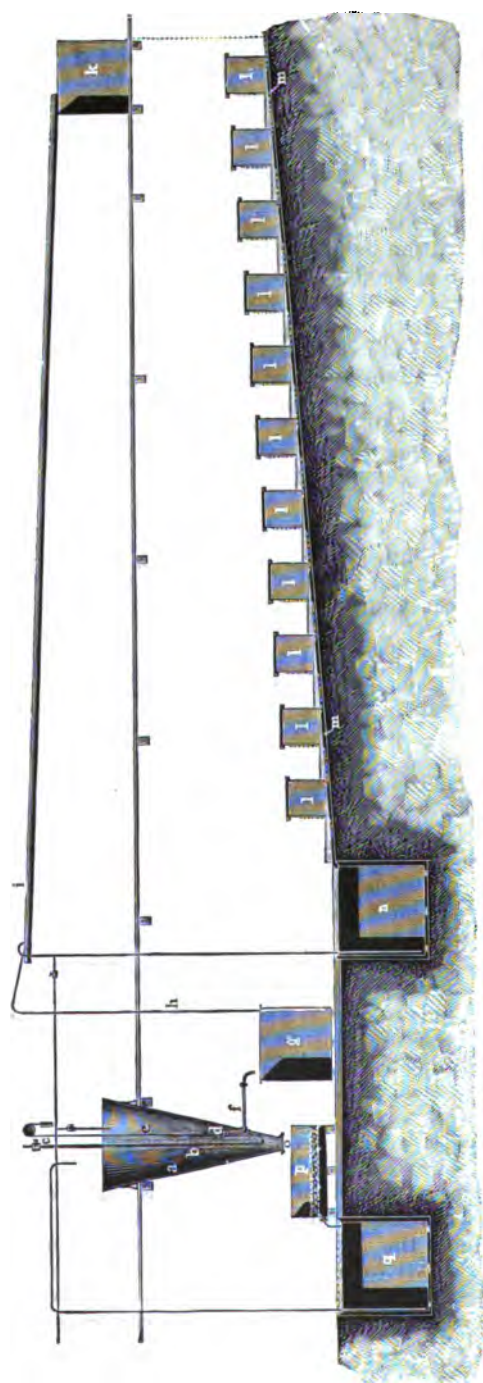
Fig. 168.—Antimony extraction plant. Section. Scale $\frac{1}{70}$.
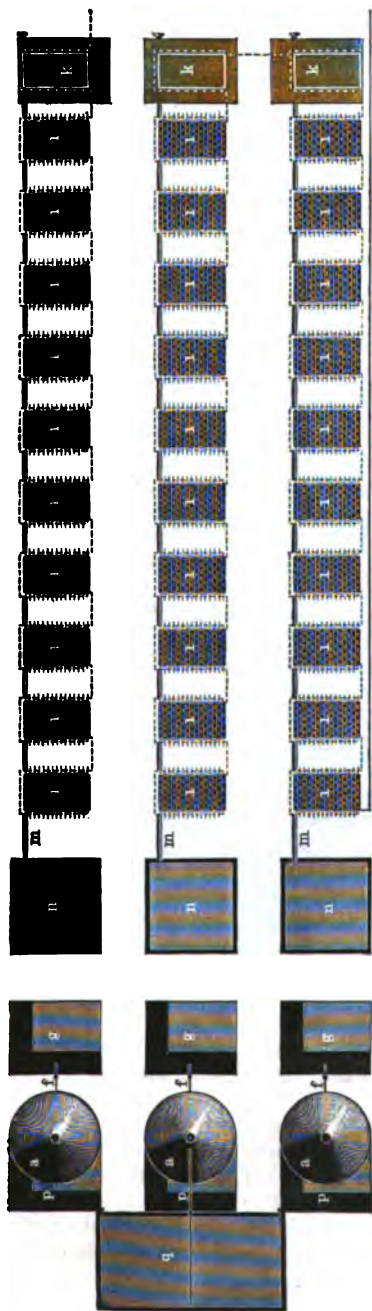
Fig. 169.—Antimony extraction plant. Plan. Scale $\frac{1}{50}$.

open below and closed above, suspended by a chain or wire, e, in such a way that it may be moved up and down over the vertical up-turned end of the pipe, f, within the leaching vessel. The height of this tube and of the bell is governed by the level at which the deposit stands within the vessel. With ores of a similar character the variations in level are not very great. By raising or lowering the bell it is possible always to draw the liquid off from just above the level of the deposit in the apparatus.

The solution is at once pumped out of the receiver, g, through the pipe, h, and the channel, i, to the reservoir, k, from which it flows through the corresponding row of electrolyte tanks, l; thence after passing through them, or when it is exhausted of antimony, it escapes through the channel, m, or the floor of the room to the tank, n, placed at a lower level, from which it may be raised for further circulation, or may be pumped to another part of the works for the recovery of thio-sulphate or of sulphur.

After this solution has been run off, the slimes in the leaching tank are again boiled up with fresh sodium sulphide liquor. The resulting solution is drawn off exactly as before, but instead of being run into the receiver, k, it is conducted to another leaching vat, a, where it is used in place of fresh sodium sulphide to treat a new charge of ore. The residue in the first vessel is then boiled up twice with a little water, which is run off into one of the receivers, g, and is used again in leaching a subsequent charge.

The exhausted slimes are then drawn off through the valve, o, at the bottom of the leaching tank into a filter, p, on which the last portions of liquid are separated, and on which the residue is rinsed with a little hot water. The wash-waters from the filters are finally accumulated in the reservoir, q, from which they are again used as extracting-water in the leaching tanks.

A plant such as that indicated in Figs. 168 and 169 on a scale of 1 : 200, would suffice for the extraction of 300 to 400 kgrm. [6 to 8 cwt.] of antimony in twelve hours from poor ores containing only 10 per cent. of the metal. By increasing the rate of working, the outturn might easily be doubled.

Single depositing tanks with their more important attachments are shown on a larger scale in Figs. 170 and 171. In the iron tanks, B, hang the replaceable anodes, A, and cathodes, K. The latter consist of iron plates, which are clamped to the square rail, T, and rest immediately on the rim of the vessel. The tank itself, therefore, is used as a cathode. In order to insulate the anodes wooden bars, J, are rested upon the brackets, H, on the long side of the upper rim of the vessel, and these carry the positive leads, P, which consist of strips of copper or iron so placed that the iron bars which carry the lead anode plates rest upon them.

The manner of circulating the solution is so clearly indicated in the drawing that very little explanation need be given. The electrolyte enters the vessel beneath, and overflows above into a channel, G, by which it passes to the next tank. This arrange-
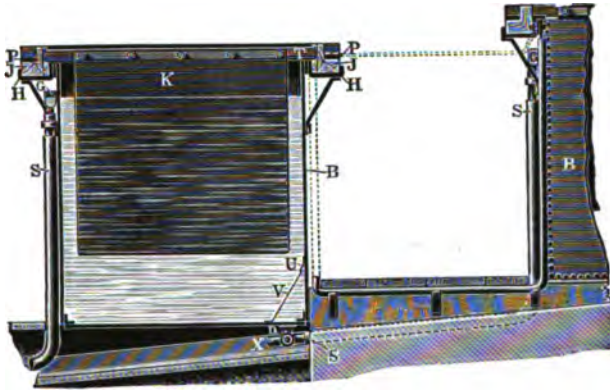
Fig. 170.—Antimony electrolytic tank. Section.
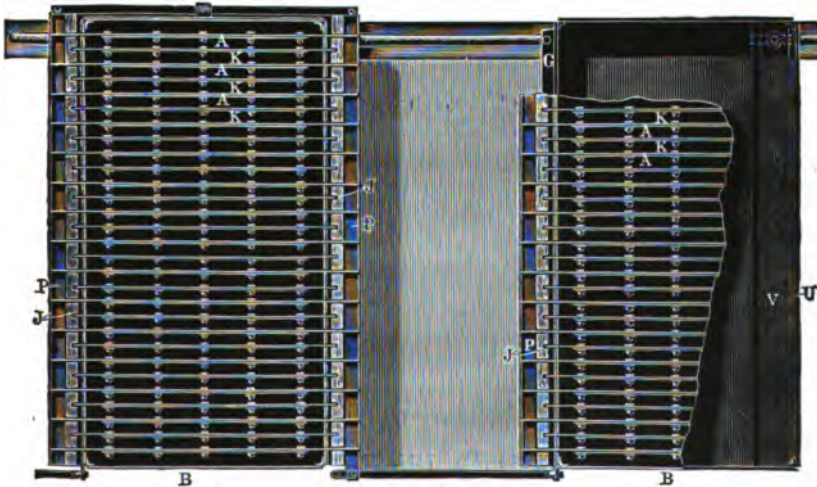
Fig. 171.—Antimony electrolytic tank. Plan.

ment must not be capable of acting as a conductor if the vessels are connected up in electrical series, and it consists, therefore, mainly of a caoutchouc tube, S. In order that the column of liquid connecting successive vats may not itself interfere with the electrical circuit, the length, and therefore the resistance, of

the column is made sufficiently great.   The solution must be introduced from below, because it becomes specifically lighter during the progress of electrolysis.   A three-way cock, D, is placed beneath the bottom of the vessel so that it may be possible to draw off the liquid through it, and through the escape-pipe, X, in connection with it.   By this arrangement it is ensured that no vessel can be emptied until connection with the one preceding has been closed.   To provide for the better distribution of the solution through the tank, a bent plate, V, is placed at the bottom of the vessel on the side of the admission pipe, and a second bent plate, U, is so attached to the side wall that there is only a small space between the two plates along the whole of one side of the electrodes.   The electrolyte is introduced through this space.   This plate, V, is riveted to the bottom, and although it is not quite water-tight, it serves to prevent the deposited antimony lying upon the bottom of the tank from being swept out with the liquid during the emptying of the tank.   In order to show this arrangement, a portion of the electrodes to the right in Fig. 171 has been cut away.   The electrical connections are clearly seen from the drawings.   The current density must decrease with the percentage of antimony in the solution. Although, with concentrated solutions electrolysis may be commenced with a current of 100 to 150 amperes per sq. metre [0·064 to 0·1 amp. per sq. in.] it is economical gradually to reduce it to about 40 to 45 amperes [0·026 to 0·03 amp. per sq. in.].   This may be effected either by introducing more baths into the circuit, or by coupling some of the tanks at the end of the series in parallel.   The necessary E.M.F. averages under two volts per bath.

The metal separates in pulverulent form or in lustrous scales according to the density of current used.   A part always settles to the bottom, whilst that which adheres to the iron plates is readily detached by steel wire brushes.   The method of melting the antimony together will be described later.

The system of working up the spent solution for sulphur or thio-sulphate may be found in the usual handbooks.

Sanderson's Process.—A few other processes which have not yet been used commercially remain to be described.   Some of them are unworkable on a technical scale.   Sanderson's [*] process for antimony refining (which, according to Vogel,[†] was experimented with by an English Company in 1889) may here be taken as a typical example.   A solution of butter of antimony in a very concentrated solution of sodium, potassium, or ammonium chloride, acidified with hydrochloric acid, is said to resist even great dilution with water ; it should, therefore, be very suitable for use as an electrolyte.   In this solution are

[*] German Patent 54,219, Feb. 26, 1890.
[†] *Zeitschrift für angewandte Chemie,* 1891, p. 327.

suspended antimony anode plates containing gold. When the current is passed they are gradually attached, the antimony being dissolved and deposited electrolytically upon the cathodes, while the gold particles sink to the bottom of the vat, whence they are removed and fused together as soon as sufficient have accumulated.

The process, however, according to Vogel's account, proved itself too costly. But apart from this, it has been shown that a chloride solution can never afford a good deposit, and even for this reason alone the process would stand condemned.

Kopp's Process.—Kopp * proposes to treat antimony ores with solutions of ferric salt, in order to obtain antimonious chloride, according to the following reaction :—

$$6FeCl_3 + Sb_2S_3 = 6FeCl_2 + 2SbCl_3 + 3S.$$

The reaction takes place rapidly and completely if free hydrochloric acid or (better) a halogen salt, such as sodium chloride, be added. The antimony solution is then to be passed into the cathode compartments of an electrolyte tank, which is divided up by diaphragms into cells, whilst the ferrous chloride solution is conducted through the anode compartments after the antimony has been deposited from it. Thus whilst the antimony is precipitated at the negative electrode, the ferrous chloride is peroxidised, and ferric chloride is regenerated at the positive electrode. The latter solution is then used once more to dissolve antimony compounds. Both anodes (!) and cathodes may be made of lead. The electrolyte is heated at 50° C., and is kept in motion. In order to obtain a dense, instead of a spongy, deposit of antimony, a current density of 40 amperes per sq. metre [0·026 amp. per sq. in.] is used.

Siemens-Halske Process. — Siemens and Halske have patented a process,† by which the sulphide of antimony, or of arsenic, is dissolved in alkaline sulphydrate and added to the cathode cells of an electrolysis-apparatus, whilst at the anodes a solution of an alkaline chloride is employed for the sake of obtaining chlorine. But this method of electrolysing thio-salts is by no means happily chosen; the recovery of chlorine at the anode is scarcely suitable here; it demands the use of a more complicated apparatus, and the introduction of diaphragms (for which no suitable material has yet been found) without offering any noteworthy advantages. The reactions quoted in the patent specification do not take place so readily as would be understood from the equation.

[This firm is now introducing into the market electro-deposited antimony, presumably made by the above process, in the form of grey plates, about $\frac{1}{32}$ in. thick, with a rough surface, covered with wart-like excrescences on one side, but smooth on the

* German Patent 66,547. † German Patent 67,973.

other (where it had been in contact with the cathode plate). The fracture is crystalline, and the metal is said to contain 99·7 to 99·9 per cent. of antimony.—TRANSLATOR.]

The electrolytic extraction of antimony has scarcely passed out of the experimental stage; but it may be assumed that, if the problem cannot be solved by the electrolysis of sulphides, it can scarcely be hoped that a satisfactory solution will be found for it.

Treatment of the Crude or Electro-deposited Antimony.—None of the methods of obtaining antimony—whether metallurgical or electrolytic—is capable of yielding a directly marketable product. Either the metal is too impure or it is obtained in a loose and pulverulent form.

A process of fusion either for *refining or for running the metal together* is, therefore, unavoidable in every case. The impurities may consist of sulphur, arsenic, iron, copper, and other metals. In order, as far as possible, to prevent the contact of the metal with iron, the impure antimony is melted in crucibles or reverberatory furnaces, in the first place with antimony sulphide (Sb_2S_3, that has been liquated from antimony glance), by which means iron and copper are principally removed, and afterwards with basic substances, such as potash or soda, together with a small proportion of oxide or sulphide of antimony. In this way the metal becomes desulphurised, with the formation of a slag containing thio-salts of antimony. The antimony obtained electrolytically and brushed off the cathodes must be washed and dried, and is then fused together under a slag of antimony oxysulphide or of thio-antimonites, with basic additions, such as soda or potash.

The Applications of Antimony have already been described in referring to its properties, they include alloying, deposition, pigments, thermo-electric couples, antimony chloride.

CHAPTER X.

CHROMIUM, MOLYBDENUM, TUNGSTEN, URANIUM, MANGANESE.

CHROMIUM.

Properties of Chromium.—Chromium (Cr; atomic weight = 52; specific gravity = 6 to 7) is a bright grey, very lustrous, and very hard crystalline metal. Its fusing point has not yet been determined with accuracy, but it is a little higher than that of platinum, or approximately 2000° C. Chromium containing

carbon melts at a temperature between 1600° and 1800° C. The alloying properties of chromium have not been so fully examined as those of other metals on account of the infusibility of the metal; and only the alloys with iron (ferro-chrome, and chrome steel) are of any practical importance. Since a metal containing carbon is yielded by most of the processes employed in extracting chromium, many of the properties ascribed in the books to pure chromium in reality belong to its carbon or carbide alloy. Pure chromium oxidises very slowly in cold air; but, on heating, the surface becomes readily covered with a thin film of oxide, which may possess any colour from yellow to blue. Even in oxygen it does not burn as readily as iron. Chromium combines with sulphur and with the halogens, evolving a very considerable amount of heat. It is especially prone to combine with carbon and silicon, and it has already been stated that it is almost impossible to obtain by simple reduction processes a metal that is free from carbon. Carbides have not yet been isolated as such; but a metal very rich in carbon is easily obtained. Carburised chromium is much harder, and resists chemical influences far more than does the pure metal. The oxide, Cr_2O_3, and the so-called chromic acid, CrO_3, are the chief compounds with oxygen that are of technical importance; the first-named forms a series of (chromic) salts with acids, the latter a series of chromates or chromic acid salts with bases.

Occurrence in Nature.—In nature chromium is mainly found as oxide in chrome iron ore, $FeO . Cr_2O_3$, which rarely, if ever, corresponds accurately to this formula, the FeO being in part replaced by MgO, and the Cr_2O_3 in part by Al_2O_3 or Fe_2O_3. Crocoisite is a chromate of lead, $PbCrO_4$. Chrome iron ore alone is practically used for the extraction of chromium.

The Reduction Process.—Chromium, which is to be used for the manufacture of iron alloys, may be reduced direct from the chrome iron ore in admixture with iron ore, either in blast furnaces or in crucibles, the product being an alloy of iron and chromium known as *ferro-chrome*. If crucibles are employed, and the alloy is to be obtained in the fused condition, it will be necessary to employ regenerative gas-firing.

. The metal can only be obtained unalloyed by treating the pure oxide, but even then it will not be free from carbon. The method of obtaining the oxide from chrome iron ore is somewhat tedious. A chromate is first obtained by calcining the finely-divided ore with potash or soda in the presence of air, and from this the oxide is produced by roasting with sulphur. The oxide formed in this way is washed free from the alkaline sulphates produced during the treatment with sulphur, and it is then reduced by heating it with carbon in plumbago crucibles. In this manner a grey metallic powder is obtained, which shows no sign of fritting even when regenerative gas-firing has been

employed. The metal can only be fused with the aid of electricity, for which purpose an apparatus heated either by means of an electrical resistance or by the arc may be used. With the aid of the former apparatus (see pp. 88, 110, 112, 113) the author was first successful in obtaining fused chromium. The simplest form of this apparatus may again be figured at this place for convenience in illustrating the principle used in heating (Fig. 172). Within the space left between the fire-bricks, A B C D F S, a mixture of chromium oxide and carbon is packed around the carbon rod, k, which forms a bridge between the thick carbon rods, K, and thus lies in the midst of the mixture. The passage of a powerful current of 8 to 10 amperes per sq. mm. of cross-sectional area of the small rod [5000 to 6500

Fig. 172.—Borchers' electric furnace.

amps. per sq. in.] is sufficient to raise the temperature of the mass to such an extent that the oxide is reduced, and the resulting chromium fuses together. The use of this furnace was explained in an earlier chapter, and it is, therefore, unnecessary to dwell further upon it here.

Moissan's Furnace.—Moissan,[*] who has described the best method of obtaining non-carburised chromium, at first recommended the use of the apparatus shown in Fig. 173. The hearth of this miniature furnace consisted of a limestone block (*pierre de Courson*), in which a rectangular cavity had been prepared. The walls of the cavity were lined with magnesia plates 10 mm. [0·4 in.] thick, and then again with carbon plates of the same thickness. Two stout carbon rods were introduced, one through each opposite side wall, the carbon lining being, of course, cut away so that it did not touch the rod at any point and so make contact with it or start an electric arc. At right angles to the electrodes, but at a somewhat lower level, a carbon tube is passed through a third wall. The tube may be set level, or at any angle of less than 30° with the horizon, and serves to contain the

[*] *Comptes Rendus*, 1893, vol. cxvii., p. 679.

substance to be heated, which either rests in or is passed through it. The end of the tube should be some 10 mm. [0·4 in.] below the electric arc. The cover of the melting chamber, like the body of the furnace, consists, first, of a carbon plate, then of a slab of magnesia, and, finally, of a limestone block.

Chaplet's Furnace.—Chaplet* seeks to distribute the heat more evenly in the furnace by submitting the tube containing
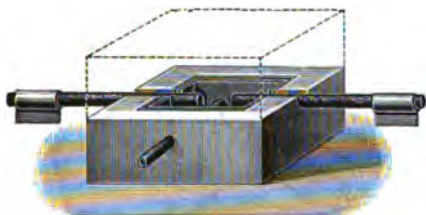
Fig. 173.—Moissan's electric furnace.
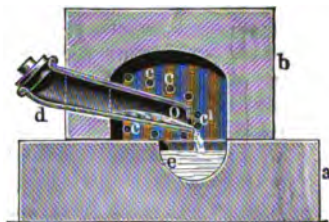
Fig. 174.—Chaplet's electric furnace.

the charge to the influence of a larger number of arcs. The furnace consists of two main portions, an under part, *a*, and an upper portion, *b*, which are luted together when in use (Fig. 174). The lower part, *a*, is in the form of a well, *e*, hollowed out of the hearth of the furnace, or extending over the whole hearth. The hearth is made to slide or to run on wheels or rollers, so that it may be moved and replaced easily. The upper part could also be made movable, so that it might be transferred from one collecting well to another.

The upper portion of the furnace contains the muffle tubes and the movable electrodes. The muffle is sufficiently inclined downwards, and may consist of a simple tube having an opening, *o*, at its lowest point, through which the molten

Fig. 175.—Chaplet's modified electric furnace.

material may flow into the collecting well. It may also be doubled, and possess a V-form with an opening at the narrow part of the V, to allow of the escape of the molten charge (Fig. 175). The electrodes, *c*, in sufficient number, are so disposed that the whole mass in the tube, *d*, may be heated. Additional electrodes, *c'*, are arranged near the mouth of the tube containing the charge, so that the arcs playing between them may prevent the solidification of the mass at this point.

* German Patent 77,896.

Refining of Crude Chromium.—Both the containing tube (whether it be made of a mixture of clay and graphite or of any other refractory material) and the carbon of the charge itself tend to prevent the formation of a pure chromium free from carbon, silicon, &c., by the smelting of a mixture of chromic oxide and carbon in an apparatus of this description. The resulting metal must therefore be refined. Moissan has ingeniously solved this problem by adapting to it the principles of the basic open-hearth steel process. By heating lime with chromic oxide he obtains a basic substance which serves for the oxidation as well as the fluxing of the impurities. If the hearth of an electric furnace be lined with this calcium chromite mixture the carbon and silicon present in the metal that is heated upon it will be oxidised and removed by the chromic oxide, in the same way that they are eliminated from iron by means of oxide of iron in the open hearth process.

Details as to the cost of this process have not yet been published. It is scarcely to be doubted that the method is capable of application on a large scale; but the author would recommend that the crude carburised chromium should be obtained in pulverulent form by reduction in crucibles or in the electric resistance furnace, in order to save the expense of fusion in the first instance.

The Precipitation Process.—The separation of chromium from its fused salts by means of zinc, and especially from chromium chloride or the double chloride of chromium, and an alkali metal was first effected by Wöhler.[*] The yield is very small, but the metal is of great purity. The alkali metals have also been used for the decomposition of chloride of chromium.[†]

ELECTROLYSIS OF CHROMIUM COMPOUNDS.

Electrolysis of Dissolved or Fused Chromium Compounds with Insoluble Anodes.—If any one work deserve to be foremost in the field of electro-metallurgy, it is that of Bunsen on the production of chromium by electrolysis.[‡] It merits especial recognition not only on account of the observation itself, and of the arrangements devised for the experiment, but because at the time at which it was accomplished, electrical energy, measuring instruments, and other requirements were not nearly so readily available as they are now. It should be pointed out to modern experimenters, to whom time or opportunity has failed for the study of the classics of electro-chemistry, that, *more than forty years ago, Bunsen showed the result of electrolysis to be dependent in many instances on the density of the current.* His account of his observations ran as follows :—

* Liebig's *Annalen der Chemie und Pharmacie*, vol. cxi., p. 230.
† Peligot in the *Ann. der Chem. und Pharm.*, vol. lii., p. 244.
‡ *Pogg. Ann.*, 1854, vol. xci., p. 619.

Bunsen's Experiments.—"The density of the current (that is to say, the relation of the strength of the current to the area of the electrode at which electrolysis is taking place) exerts the most important influence on the resulting chemical reactions. Thus, for example, if a current of unvarying strength be passed through a solution of chloride of chromium in water, it depends upon the surface area of the electrode at which reduction is effected, whether hydrogen, chromic or chromous oxide, or metallic chromium shall be obtained.

"Not less important is the relative mass of the constituents of the electrolyte through which the current is passed. Thus, if with a constant current density the proportion of chloride of chromium in the solution be gradually increased, a point will soon be reached at which the separation of chromous oxide will be accompanied, and this will presently be succeeded, by a reduction of the metal.

"As unit of current density, I adopt that of a current of which the absolute intensity is 1 on the surface of 1 sq. mm. The density, D, will then depend upon the absolute intensity, I, and the area, O, of the polar surface measured in sq. mm., thus

(1) $D = \dfrac{I}{O}$; I is found with the aid of the tangent galvanometer

from formula (2) $I = \dfrac{RT}{2\pi}$ tan φ, in which R is the radius of the galvanometer ring in mm., φ is the angle through which the galvanometer needle is deflected, and T is the horizontal component of the earth's magnetism (Gauss' measurement). In this formula, T requires a special adjustment according to time and place. This is most simply and accurately determined by the electrolysis of water, basing the calculation upon the known electro-chemical equivalent of water. If the quantity of water decomposed by the current, I, in t seconds be termed A, and the known electro-chemical equivalent, or the weight of water decomposed by an unit of current (in Gauss' measure), be called

α, then according to Faraday's law (3) $I = \dfrac{A}{\alpha t}$. Now, by combining this with equation (2), it will be seen that

$$T = \frac{2\pi A}{\alpha t R \tan \varphi}.$$

"In order to obtain the highest current density to overcome powerful (chemical) affinities, I use a decomposing cell, of which one pole is formed by the inner surface of a carbon crucible, that stands within a porcelain crucible, and is filled with hydrochloric acid, and kept hot by means of a water bath. A small clay cell stands within this, and contains the solution to be decomposed and a small platinum strip, which forms the other pole; the

current flowing radially from the walls of the crucible is con-
centrated to a great density upon the surface of this platinum
pole. In this miniature arrangement, chromium, manganese,
and many other metals may be reduced from their chlorides with
the greatest facility.

"The density of the current in one of these experiments is
determined from the following elements :—

$$R = 201 \text{ mm.}; \ T = 1\cdot 870; \ \varphi = 42°15'; \ O = 811 \text{ sq. mm.}$$

$$\therefore \ D = \frac{RT}{2\pi O} \tan \varphi = 0\cdot 067.$$

"The reduction of the metal, therefore, followed from the
electrolysis of the concentrated solution of the sub-chloride
heated to the boiling temperature, while every sq. mm. of sur-
face of the reducing pole received a current of the absolute
intensity of $0\cdot 067$ units.

"If the current density be gradually reduced, a point is soon
reached at which the reduction of metal no longer occurs, but is
replaced by a plentiful deposition of chromo chromic-oxide.
This compound can only be thus produced in large quantity,
and may be obtained pure by prolonged boiling with aqua regia."

The author has frequently repeated this experiment and, for
the purpose of obtaining larger quantities of metal, has altered
the conditions of the experiment within certain limits, but has
always obtained satisfactory results by working within the
limits of current density named, and by using a high degree of
concentration in the cathode cell. According to modern units
of measurement, the current density should be about 700
amperes per sq. metre [0·45 amp. per sq. in.] of cathode surface.
The following is an account of the author's experiments :—

Borchers' Experiments. — A capacious stoneware vat is
filled with a solution of sulphurous acid or of sodium bisulphite,
and in this solution is placed a large carbon plate. Instead of
the clay cell filled with solution of chloride of chromium, a linen
bag is employed, charged with a thick paste of chloride or
fluoride of chromium crystals, mixed with hydrochloric acid,
and containing a platinum plate. It would seem that in pro-
portion as the paste is thicker and more sluggish, the more
readily a current of 700 to 800 amperes per sq. metre [0·45 to
0·52 amp. per sq. in.] affords the metal, which is deposited in
the crystalline state upon the cathode. The E.M.F. required in
this case is about 8 to 10 volts. The process is, therefore, not
likely to be applied on a technical scale. But apart from the
high E.M.F. necessary for the decomposition, other objections
to the process are found in the rapid heating of the solution and
the evolution of large quantities of acid vapour.

The Placet-Bonnet Process.—For the sake of completeness

reference must be made to the process of Placet and Bonnet, which has been patented in most countries, and by which several ingots of chromium shown in the American Exhibition were said to have been made. According to one of the patent specifications,* the electrolyte is prepared by warming a mixture of 100 parts by weight of water, with 100 of chrome alum, and 10 to 15 potassium bisulphate. The electric current (details as to the strength, pressure, and density of which are not given) at once deposits chromium upon the cathode. The original strength of the solution is maintained by the addition either of chrome alum alone, or of a strong solution of chrome alum and alkaline bisulphate. An overflow tube attached to the electrolysis tank serves to keep the level of the solution at a constant height. If chrome alum alone be added to the bath, a time will arrive at which all the water of the solution, together with the salts that are dissolved in it, will have passed away through the overflow pipe. The electrolyte now consists of salts which can be liquefied either by water or by heat. Water is no longer necessary, and the mass of salt is consequently heated to its fusing point. Potassium chlorate and boric acid, benzoic acid, or "analogous salt," are now to be added to the fluid mass at intervals. As a substitute for potassium bisulphate, there may be used as a flux either the sulphate or the bisulphate of soda or ammonia, the phosphate, borate, chlorate, silicate, chloride, fluoride, &c., of the alkalies or alkaline earths, or mixtures of these salts; and in lieu of chrome alum any other easily fusible chromium salt may be employed. Since a very high temperature is necessary for the fusion of chromium, an electric current is "ordinarily" used for the purpose. The electrodes may be compressed mixtures of carbon and chromium oxide or salts, with reducing and fluxing agents, or they may be composed of metals such as copper, aluminium, zinc, nickel, silver, &c., or of oxides of these metals (e.g., alumina electrodes!). In the latter case chromium alloys are obtained. The inventor recommends also that neutral or reducing gases, or metallic powders (such as zinc or aluminium) be blown through hollow electrodes during electrolysis. Any serious criticism of the above is obviously superfluous.

The electrolysis of the oxide dissolved in fused metallic salts, which was proved to be a valuable method in the case of aluminium, is hardly applicable to chromium on account of the very infusible character of the metal. But if it be desired solely to produce a chromium free from carbon, for the purpose of alloying it subsequently with other metals, either the fused chloride may be electrolysed or other chromium compounds, that are soluble in the salts, referred to in the Chapter on *Aluminium.* An easily fusible *alloy of chromium and*

* English Patent 6751, 1893; U.S.A. Patent 526,114.

aluminium may thus be obtained in the apparatus shown in Fig. 86, and described on p. 157. The process is conducted exactly as in the reduction of aluminium, and when electrolysis has been started the apparatus is charged with a mixture of alumina and chromium oxide, or fluoride, &c. Since the fusing points of the whole series of aluminium-chromium alloys have not yet been determined, it is impossible to name the limit of chromium which may thus be alloyed with aluminium.

Electrolysis of Fused Salts with Crude Chromium or Ferro-Chrome Anodes.—Chromium Refining.—The only instance of this method of obtaining chromium is that described in a patent specification* of the firm of Frederic Krupp, of Essen. The sole intention is to produce chromium free from carbon; and no attempt is made to prevent the production of a metal containing iron, or of a ferro-chrome. For this purpose the double chlorides of the metals named above, with the haloid salts of the former metals, are electrolysed with anodes of ordinary carburised ferro-chromium. The metal deposited on the cathode is entirely free from carbon. It would appear from the specification that the process is not so simple as would seem at first sight, for diaphragms have to be used to separate the anode and cathode compartments. No process, however, in which it is necessary to use clay cells in the electrolysis of fused salts, can have much prospect of being adopted on a large scale.

The **Application of Chromium** is restricted almost entirely to the iron industry, in which the metal is employed in the pure state or in the form of ferro-chrome, for the production of chrome steel.

MOLYBDENUM.

Properties and Occurrence of the Metal.—Molybdenum (Mo; atomic weight = 96; specific gravity = 8) is a white, extremely lustrous, and very hard metal, which it has hitherto been exceedingly difficult to obtain pure in the fused condition. Its melting point apparently approximates that of chromium, and should therefore lie between 1800° and 2000° C. The alloys of molybdenum have not yet been studied, but in respect of solubility in other metals it appears to resemble chromium.

In the air it begins to oxidise at high temperatures. Acids scarcely affect molybdenum, with the exception of nitric acid which converts it into oxide or molybdic acid. Of the numerous oxygen compounds the trioxide, MoO_3, the so-called molybdic acid, is the most important and the most readily produced; it is acid in character. The sulphides readily form thio-salts with alkaline sulphides. All the oxides possess characteristic colours.

* German Patent 81,225.

Among the compounds chiefly found in nature, the sulphide, MoS_2 (Molybdenite), and the molybdate of lead, $PbMoO_4$ (Wulfenite), alone are used for the production of molybdenum and its compounds.

The Production of Molybdenum is always effected by reduction. Wöhler and von Uslar succeeded forty years ago in reducing the trioxide by heating it in a current of hydrogen. The oxide may also be reduced by electrically heated carbon, and the metal is thus rapidly and easily obtained in the molten condition, but it always contains carbon. The apparatus and the method of using it are the same as for chromium and its alloys.

Molybdenum steel has been made, but the material has not yet found any special application.

TUNGSTEN.

Properties of the Metal.—Tungsten (W; atomic weight = 184; specific gravity = 19) forms a grey crystalline powder, or after fusion, an almost white, very lustrous and hard metal. Its fusing point cannot be quite as high as those of molybdenum and chromium, although it is commonly reported to be so, for the author has succeeded in fritting the powdered metal together in a regenerative gas furnace, at a temperature sufficiently high to cause the softening and collapse of the best Hessian crucibles, while powdered chromium and molybdenum introduced at the same time remained quite dry and unfused. The only alloys of tungsten that have been studied are those with iron; these have found special applications in the steel industry. Tungsten only begins to oxidise at elevated temperatures when heated in the air. Of the two simpler oxides, WO_2 and WO_3, the latter (the trioxide or tungstic acid) is most easily formed; it is acid in character. The trisulphide, WS_3, also functions as an acid readily forming thio-salts with other sulphides, those of the alkaline sulphides being soluble in water. Among the naturally occurring compounds of tungsten are—tungstic ochre, WO_3; scheelite, $CaWO_4$; and wolfram, $FeWO_4$. The latter mineral frequently accompanies tinstone, a fact that was mentioned in the Chapter on *Tin*.

The Extraction of Tungsten is accomplished almost exclusively by simple reduction. The production of iron tungsten alloys is the simplest case, for then the ore (wolfram) may be employed directly, and may be simply fused, with carbon, glass, and the necessary scrap-iron, in plumbago pots, heated in a regenerative gas furnace. Pure metal can only be obtained from the pure trioxide. Tungstate of soda (Na_2WO_4), is first formed by calcining the ores (or tin slags) with soda; this

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salt is then dissolved in water and purified from insoluble
substances by filtration, and from soluble impurities by re-crys-
tallisation. The tungstate is decomposed by hot hydrochloric
acid, which causes the separation of a heavy yellow precipitate
of tungsten trioxide. This is washed, dried, mixed with wood
charcoal and a little rosin, placed in a clay crucible, and then
reduced at the temperature of the ordinary wind furnace. In
this way a grey metallic powder is obtained, which will be found
sintered together, if a regenerative gas furnace be used. By
electrical heating (either by a resistance or by the arc) the
tungsten may be readily brought to fusion.

The electrolysis of aqueous solutions of the thio-salts of
tungsten has not given satisfactory results in the author's
hands. The possibility of electrolysing tungsten compounds
dissolved in fused salts is practically excluded by the high
fusing point of the metal, unless aluminium, or some other
metal which forms readily fusible alloys with tungsten, be
present. The explanation of this latter method has already
been given in the Chapter on *Chromium*.

Tungsten and its alloys are used almost exclusively in the
steel industry.

URANIUM.

Properties of the Metal.—Uranium (U ; atomic weight = 240;
specific gravity = 18·6), like the members of the chromium group
already described, is a white, lustrous, and hard metal of high
fusing point (not yet accurately determined). It oxidises in the
air only at relatively high temperatures. Hydrochloric, warm
dilute sulphuric acid, and nitric acid are solvents for uranium,
but the last named is only available for the treatment of pulver-
ulent metal. Some of the oxygen compounds are employed as
pigments, the simpler oxides are UO_2 and UO_3, of which the
latter is found both as base and as acid. The only noteworthy
ore is Pitchblende (Uraninite) which is a urano-uranic oxide
U_3O_8 ($= UO_2 . 2UO_3$).

More than 40 years ago Peligot[*] proposed the decomposition
of the chloride by alkali metals. According to the majority of
chemical text-books, the oxide cannot be reduced by carbon.
The author has, however, succeeded in reducing this oxide, in
common with many others that were considered to be non-
reducible, by electrically heated carbon. This observation was
noted in the previous edition of this book (in 1891), and since
then it has been confirmed by Moissan.[†] The arrangements
for the reduction process have already been described several
times in this work.

[*] *Annalen der Chemie und Pharmacie*, vol. xcvii., p. 256.
[†] *Comptes Rendus*, 1893.

The metal is of no technical importance. It, however, affords
an additional proof of the law laid down by the author that *there
is no metal incapable of being reduced by carbon.*

MANGANESE.

Properties of the Metal.—Manganese (Mn; atomic weight
= 55; specific gravity = 7 to 8) is a white, lustrous metal with
a slightly reddish tint. It is very hard and brittle, and melts
between 1200° and 1500° C., but its exact fusing point has not
yet been determined. Of its alloys the best known are those
with iron—*ferro-manganese* and *spiegeleisen*—and with copper—
manganese bronze. It is capable of alloying also with chromium,
aluminium, tin, mercury, silver, and the other noble metals.
Chemically, manganese is a very active element. It oxidises
readily in the air* at ordinary temperatures, and should, there-
fore, be kept under paraffin oil. It readily combines with the
halogens, as with sulphur, phosphorus, carbon, silicon, and boron.
Water also is readily decomposed by manganese at ordinary
temperatures. It dissolves readily in all inorganic, and in many
organic, acids, usually with evolution of hydrogen, and always
with the formation of manganous salts. Alkaline hydroxides,
especially when oxidising agents are present, dissolve manganese,
forming manganites, manganates, and permanganates. Among
the oxygen compounds the manganous oxide, MnO; manganic
oxide, Mn_2O_3; and mangano-manganic oxide, Mn_3O_4, are basic in
character, yielding manganous or manganic salts, in which
manganese is present in the form of base. The binoxide, MnO_2,
the so-called manganic acid, MnO_3 (not known in the uncom-
bined state), and the heptoxide, known also as permanganic
acid, Mn_2O_7, function as acids. They unite with bases to form a
series of salts, many of which are of considerable value in the
arts. The binoxide forms manganites (*e.g.*, $CaMnO_3$), man-
ganic acid gives manganates (*e.g.*, K_2MnO_4), and the heptoxide
yields permanganates (*e.g.*, $KMnO_4$).

Occurrence in Nature.—Manganese occurs chiefly in the
form of oxides, of which the binoxide or pyrolusite, MnO_2, is the
most important, the oxide, Mn_2O_3, is found in braunite, the man-
gano-manganic oxide, Mn_3O_4, in Hausmannite, the hydroxide,
$Mn_2O_2(OH)_2$, in manganite; a sulphide in Hauerite, MnS_2; salts in
dialogite (rhodochrosite), $MnCO_3$, rhodonite (manganese silicate),
and in psilomelane, which is a complex manganite containing
manganese oxide, baryta, and potash with manganic binoxide.

* [It has recently been shown that fused manganese, when pure, is far
less oxidisable in the air than is generally supposed. The carburised
manganese is most readily attacked, and it gives rise to disintegration,
owing to the mutual decomposition of the moisture of the air and the
carbide.—TRANSLATOR.]

The choice of an ore for smelting purposes depends upon whether it is intended to produce metallic manganese or a manganese alloy. Usually the alloy is required, because manganese [as prepared] is not sufficiently permanent in the air, and has not sufficient applications in the arts to warrant the erection of a plant specially for its manufacture. For the preparation of spiegeleisen and ferro-manganese, manganiferous iron ores and mixtures of iron and manganese ores may be used.

Reduction of Manganese.—The extraction of manganese is effected solely by reduction. For *spiegeleisen* and *ferro-manganese* manganiferous iron ores (spathic ores after calcination) or manganese oxide ores, mixed with easily reducible iron ores, are smelted with the necessary fluxes in blast-furnaces (almost exclusively so now), or in crucibles, the fluxes being so proportioned that a manganiferous basic slag—which must, at the highest, be a mono-silicate—shall be produced. When the metal contains from 5 to 20 per cent. of manganese it is termed a spiegeleisen; with more manganese, which may range up to 85 per cent. in the product of the blast furnace, it is known as ferro-manganese. These alloys, in addition to varying percentages of silicon, always contain from 4 to 7·5 per cent of carbon.

Manganese (unalloyed with iron) may be prepared by smelting an intimate mixture of carbon with the pure oxide, which is readily obtained commercially. In this case the mixture must either be packed in crucibles placed in regenerative or wind furnaces, or in electric furnaces heated by a carbon resistance.[*] This process must of necessity yield a metal containing carbon and silicon, for manganese exerts a powerful solvent effect upon carbon.

The Precipitation Process.—Manganese may be produced by the action of the alkali metals upon its haloid salts.[†] But for technical purposes this method is of no importance.

ELECTROLYSIS.

The Electrolysis of Dissolved or of Fused Manganese Compounds with Insoluble Anodes.—In the Chapter on *Chromium* an account was given of the work of Bunsen in 1854, and of his opinion that, given a high current density, manganese and other metals, as well as chromium, could be separated from the aqueous solution of the chloride. The author is able to confirm what was written in that chapter, but must add that it is so exceedingly difficult to free the deposited metal from the solution adhering to it that the manganese can be kept only for a short time unattacked. The process, therefore, is not technically applicable.

[*] *Cf.* pp. 88 and 110-114.   [†] *Pogg. Ann.*, 1857, vol. ci., p. 264.
[‡] *Comptes Rendus*, vol. xliv., p. 632.   [§] *Pogg. Ann.*, 1854, vol. xci., 619.

In order to obtain pure manganese it would be possible to proceed exactly as in the case of aluminium, for the melting point of the metal would permit of the application both of this method and of the apparatus already described under *Aluminium*, and here again illustrated (Fig. 176). In this case a mixture of fluorides and other non-volatile salts, with manganese oxide, would be maintained in a state of fusion by a current of
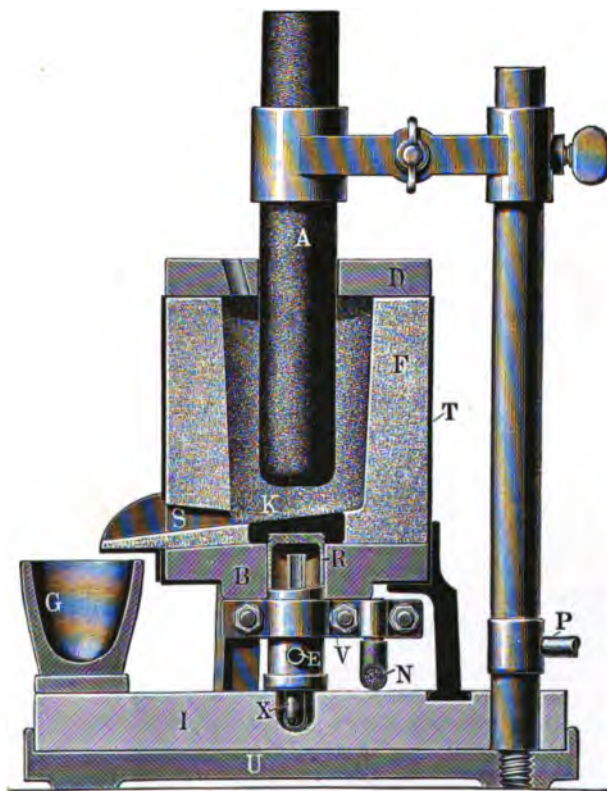
Fig. 176.—Borchers' electric furnace.

high density, and would, at the same time, be submitted to electrolysis. The operation would be conducted exactly as in the reduction of aluminium, only at a higher temperature; and it is conceivable that a steady production of fused manganese might be maintained after this manner. In any case, aluminium alloys might readily be so produced, and these would, under some circumstances, serve the purposes to which the pure metal was to be applied.

Electrolysis of Fused Manganese Compounds with Soluble Anodes.—In a process proposed by Voltmer haloid salts of manganese are to be electrolysed in the fused state with anodes of manganese oxide and carbon, unless it were preferred to add the manganese oxide direct to the fusion during electrolysis. Anodes of oxides and carbon have never been successful since their use was proposed by Deville; the cause of the failure was explained at length under *Aluminium*. The operation is so conducted, according to the specification, that the manganese separates as a crystalline powder, which is then to be pressed and washed to separate the electrolyte still clinging to it. But owing to the oxidisability of the manganese, this last operation would give rise to great difficulties, even if it could be accomplished satisfactorily.

The process of Friedr. Krupp, of Essen, by which ferro-manganese is to be used as the anode in a bath of fused manganese salts, has already been described in the Chapter on *Chromium*.

Applications of Manganese.—Manganese is principally used in the iron industry in the form of spiegeleisen and ferro-manganese for the desulphurisation of pig-iron, and for the recarburisation of steel.

CHAPTER XI.

IRON.

The Properties of the Metal.—The metal known in everyday life as iron is never pure iron, but always consists of an alloy in which this metal is the principal constituent, but which also contains the following substances in varying proportions:— Carbon and carbides of iron, silicon and silicides of iron, oxide, phosphide, and sulphide of iron, manganese, chromium, tungsten, nickel, copper, &c.

Chemically pure iron has an atomic weight of 56 and a specific gravity of 7·86; it possesses a greyish-white colour, and shows a high lustre on polished surfaces. At ordinary temperatures it is magnetisable. Its melting point is about 1600° C., and it is capable of alloying with most metals, even if its solubility in some cases be somewhat limited. It remains for a long time unaltered in dry air, but, when the latter is moist, it oxidises rapidly even in the cold. At high temperatures it is oxidised even by dry air, as well as by oxygen, and by steam, the latter being decomposed by the metal. Most of the metalloids combine more or less readily with iron, some—the halogens—at ordinary

temperatures. It is easily soluble in most dilute mineral acids, and with difficulty in strong acids, but remains almost insoluble (passive) in strong nitric acid, in consequence of the formation of a superficial coating of oxide. The more important compounds of iron are derived from the protoxide (ferrous oxide), FeO, and the peroxide (ferric oxide), Fe_2O_3; a third oxide, Fe_3O_4, is in itself of considerable importance, but when treated with acids it yields only ferrous and ferric compounds. Another oxide, FeO_3, is not met with in the free state, but, acting as an acid, it is known as ferric acid, and combines with bases to form ferrates, which, however, are readily decomposed.

The melting point, hardness, structure, and other physical properties are mainly affected (but the chemical properties only in a small degree) by the presence of the constituents named above as being present in commercial samples of iron. This is not the place to describe the influence of each foreign element upon the metal; but the following short account of the commercial varieties of iron will suffice to show that carbon plays a most important part in the metallurgy of this metal :—

1. **Pig-Iron and Cast-Iron.** — With at least 2·3 per cent. of carbon; melting point between 1075° and 1275° C.; non-malleable.

(a) *White Iron.*—Cast iron solidified without any separation of carbon; silver-white, lustrous, brittle, very hard, forming the raw material from which malleable iron may be made.

(b) *Grey Iron*, or cast iron, from which some of the dissolved carbon has separated in the form of graphite on solidification; it has a crystalline structure, and a grey or black fracture, the colour being due to the graphite plates lying between the crystals; it is the principal raw material of the foundry, and is also a source of malleable iron.

2. **Malleable Iron and Steel.**—With at most 1·6 per cent. of carbon; the fusing point lies between 1400° and 1700° C.; the metal is malleable.

(a) *Steel.*—A malleable material which is capable of being hardened almost to brittleness by heating it to a red heat and then suddenly cooling it. It melts between 1400° and 1600° C.

(b) *Malleable Iron.*—A malleable metal scarcely capable of being hardened by quenching, and melting between 1600° and 1700° C.

As will be seen in the short sketch given below, in some methods of manufacture the malleable iron never becomes perfectly fluid; but it crystallises out of the impure (but easily fused) melted cast iron, so that for the formation of a solid mass the *pure iron crystals that have separated must be welded together under the hammer*. Malleable iron produced in this manner is known as *wrought iron* or *weld iron*; and steel similarly made is sometimes termed *weld steel*. In other processes the iron

remains fluid throughout the period of refining, and the finished
material is occasionally classified as *ingot iron* or *ingot steel.* In
a third type of process cast iron articles are converted into
malleable iron without change of form by a process of annealing
in oxide of iron ; and the product is known as *malleable cast iron*
[or often in the trade merely as "malleable iron"]. Wrought
iron that has been carburised without alteration of shape is
called *cement steel.*

Occurrence of Iron in Nature.—*Native iron,* as an original
constituent of the earth, is but rarely found ; but large masses
(up to 25 tons in weight) of meteoric iron that have fallen from
extra-terrestrial sources are sometimes met with. Oxides of
iron are found in the following ores :—Iron glance and red
hæmatite, Fe_2O_3; magnetite or magnetic iron ore, Fe_3O_4; limonite,
brown hæmatite, minette, $Fe_2O_2(OH)_2$ to $FeO(OH)_4$. Of sulphides,
the principal is iron pyrites, FeS_2, which is employed for the
manufacture of sulphuric acid ; after roasting, the calcined
product (purple ore) is occasionally, but very rarely, smelted in
blast furnaces. The chief salts employed in the iron industry
are spathic iron ore, $FeCO_3$, and vivianite, $Fe_3(PO_4)_2$. The above
ores may contain silica and silicates, calcium carbonate,
manganese oxide and carbonate, oxide of chromium, alumina,
&c., which must be taken into account in the smelting of the
metal.

Among the waste products of the iron or other industries
that are utilised in the extraction of iron, the most important
are the slags from the refinery and mill furnace (which consist
of basic silicates rich in iron), metal scrap, and the burnt pyrites
already referred to.

Preparation of the Raw Materials.—Many of these ores
and products may be used directly, and only in special cases is
mechanical, chemical, or (generally after preliminary chemical
treatment) magnetic preparation necessary. The mechanical
preparation consists either in simply crushing the larger lumps
of ore to pieces of convenient size, in washing away sandy or
clayey portions, or in binding together fine-grained particles
with the aid of a cementing medium and a press. The heating
or burning of a dense ore merely to render it more open is now
rarely resorted to. Chemical preparation consists in calcination
for the dissociation of spathic ores for the conversion of this
ore or of magnetic iron ore into the more readily reduced per-
oxide, or for the conversion of spathic iron ore, or peroxide into
ferro-ferric oxide, when it is required subsequently to treat the
material magnetically.

Magnetic Separation.—The electro-magnetic separation of
ores containing iron affords the first opportunity of applying
electricity to the extraction of iron; and it should be noted
that, of late, the technical journals and the daily press have

frequently confounded this process with the electrolytic extraction of iron. No electrolytic process for the extraction of this metal is, however, practicable at present, owing to the low price of the latter, and to the fact that the heat employed in smelting iron by purely metallurgical methods is very thoroughly economised in most works.

The principles of magnetic separation are in all cases as follows: —The mixture of magnetisable and non-magnetisable particles of the ore is so moved through a magnetic field that the path of the former particles is altered by the attraction of the magnet, whilst that of the latter is unchanged; hence the apparatus delivers the two classes of material into separate receptacles. In order to attain this end a large number of different forms of apparatus have been constructed; indeed, in the United States alone more than 170 patents have been granted for magnetic separators. It is, therefore, impossible here to enter into the details of construction or principles of these machines, and it must suffice to describe in quite general terms the method adopted in some of the plants employed.

Magnetic separation has only been applicable when the iron was present in the form of ferro-ferric oxide, Fe_3O_4, or of metal. The process is, therefore, most simply applied when, as in California, ores or sands containing magnetic oxide of iron occur. So, also, heaps of this class of ore that have been stocked for years have been treated. The sand or raw ore (the latter after it has been crushed and screened) can, in this case, be passed directly through the separator. The treatment of ores, in which the iron is present in the form of non-magnetisable compounds, requires a preliminary calcination to ferro-ferric oxide. At Allevard (Savoy),* spathic ores are thus separated from such gangue stuff as sandstones or crystalline schists, by combining a calcination in kilns and subsequent magnetic separation, with a system of mechanical preparation that would otherwise have but little value.

An installation at the Friedrichsegen Mine at Bad Ems† has given excellent results since 1880 in the treatment of zinc and lead ores containing spathic iron ore. Favourable reports‡ are also given of a plant which was put down by Ferrares at the Monteponi Mines for an almost identical purpose. In this instance there was an accumulation of slimes from the older dressing processes; these slimes contained 26 per cent. of zinc ore with about 10 per cent. of ferric oxide, and hitherto had been quite unmarketable. After roasting in revolving calciners to convert the peroxide into the magnetic oxide of iron, the

* Lürmann in *Stahl und Eisen*, 1894, p. 618.
† Leo in *Zeitschrift für Elektrochemie*, 1894, p. 393.
‡ *Engineering*, 1894, vol. lviii., p. 518; *Zeitschrift für Elektrochemie*, 1894.

slime is treated by a combined system of mechanical and magnetic separation. Leo,* in a valuable article in the *Zeitschrift für Elektrochemie*, describes numerous other installations which have been made for the recovery or separation of iron compounds from ores and from heaps of old tailings.

The Smelting of Iron.—The processes of iron extraction may be divided into two groups, concerned with either the production of crude iron, or the conversion of crude into malleable iron. The direct extraction of malleable iron from the ore was the original process of smelting, but it is now mainly practised in a few uncivilised countries.

Production of Crude Iron.—In all civilised countries, the crude iron is produced by smelting oxidised ores of iron with fluxes (usually limestone) in blast-furnaces. The reduction of the oxide in these furnaces is effected mainly by carbonic oxide, but in part by the coke which serves both as a reducing agent and as a heating material. It is impossible to prevent the iron so obtained from taking up a number of impurities which entirely unfit it for hammering, rolling, welding, and the like; although indeed it is for some purposes desirable that they should be so introduced. The product of the blast furnace is therefore an alloy of iron with manganese, carbon and carbides, silicon and silicides, iron phosphide, sulphide and oxide, often with other metals such as copper and chromium in addition.

It has many times been proposed to substitute an electrical smelting process for the treatment of iron ore in the blast-furnace; but the inventors have for the most part built their hopes upon insecure foundations, inasmuch as they have compared the text book accounts of the blast-furnace practice of half a century ago with the results that are to be expected from the application of the most recent inventions in electro-technics.

De Laval's Smelting Furnace.—The smelting furnace of De Laval is not ill-adapted to the smelting of metals in general. The inventor † recommends that the iron ore with the usual reducing agent should be so heated that the reduced metal is not actually fused. The melting of the metal by electrical means renders any further refining process unnecessary, and is effected in a low shaft furnace, shown in Fig. 177, in vertical cross-section, in Fig. 178, in horizontal section, and in Fig. 179, in vertical longitudinal section. The hearth is divided into two small compartments by a bridge, C, fitted with a cooling arrangement, C'. In these compartments are laid the electrodes, D and E. In starting the operation, the fused electrolyte, I, is poured through the opening, B, in the cover of the shaft, A, and at the same time the electrodes, D and E, are connected up in a powerful electric circuit. The resistance of the electrolyte must be so

* *Engineering and Mining Journal* (New York), 1894, vol. lvii., p. 509.
† *Ibid.*

great that the bath is maintained at the melting temperature by the direct conversion of electricity into heat. An alternating current is used in order that the electrolyte (*e.g.*, magnetic iron ore) may not be decomposed. The metal to be used is introduced through B, and, falling into the bath, becomes melted and collects in the two electrode chambers, where it accumulates until it has attained a sufficient depth to cause it to flow away through F or G. The level of the electrolyte is kept constant by means of the opening, H. The cooling arrangement consists of a hollow flat inverted metal trough, C, with the openings, C_2 and C_3, through which the cooling liquid is introduced or removed.

Fig. 177.
Vertical cross-section.

Fig. 178.—Horizontal section.   Fig. 179.—Vertical longitudinal section.
De Laval's electric furnace.
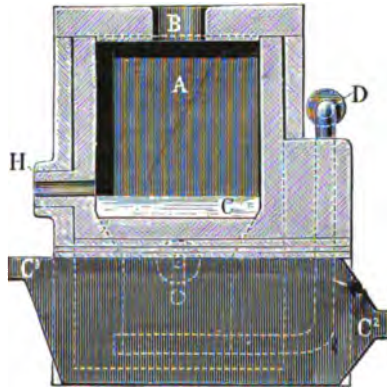
No results of any practical trials of this furnace have yet been published.

The Production of Malleable Iron.—In order to convert the crude iron into malleable iron, it is necessary to remove from it those constituents which interfere with the valuable properties of the pure metal. This is accomplished in most cases by reducing the proportion of every foreign substance almost to zero, and then, if necessary, restoring to the metal in suitable quantity those elements which may be required to give to it the special

qualities sought. The separation of the impurities is always effected by oxidation, either with or without fusion. The oxidising agent is sometimes atmospheric oxygen, sometimes oxide of iron — especially the magnetic oxide — either added directly as such, or resulting from the oxidation of iron by the air. The processes of oxidation may be divided into :—

(a) **The Finery.**—This is only used exceptionally on account of the costliness of the charcoal which is the fuel employed. It may be pictured as a large smith's fire, of which two sides are freely approachable. In the first stages of the process pig iron is melted down by means of a charcoal fire in a shallow hearth. Later the iron becomes less fluid, and always, as the impurities are removed by means of the added oxides (slag rich in protoxide of iron), the metal becomes thicker until at last it can only be worked with considerable difficulty. In order to produce steel in this hearth, pieces of spiegeleisen are added to produce recar-burisation. The metal finally obtained is hammered to unite the particles of iron which are interpenetrated with slag; it is then trimmed and hammered into bars 2 in. square. This process gives, therefore, a weld iron or weld steel.

(b) **Puddling.**—The puddling furnace is of the reverberatory type, fired with solid fuel or (either in part or entirely) with gaseous fuel. The pig iron is melted at a high temperature under a bath of slag, and is then rabbled with iron bars with free access of air at a slightly lower temperature. After breaking up and working the mass, which constantly becomes thicker and stiffer in spite of an increased temperature, the iron is worked up into from four to six balls, which are then squeezed to weld the iron particles together and to press out the enclosed cinder, and are formed into rectangular bars under the steam hammer, and rolled. This process, therefore, also affords a weld iron or weld steel.

(c) **The Bessemer and** (d) **Thomas-Gilchrist Processes.**— In these processes the iron in a fluid condition is treated with air in a vessel known as the Bessemer converter, the air being forced through the liquid metal at the bottom of the vessel. The impurities present in the iron serve as fuel, and by their oxidation produce so much heat that the charge remains melted, and the temperature at the end of the flow is considerably higher than that at the commencement. After pouring off the slag the metal, which has been somewhat over-blown, is deoxidised by the addition of spiegeleisen or ferro-manganese, and recarburisation to the desired degree is then effected either by the use of a sufficient quantity of powdered coke in the casting-ladle into which the finished metal is poured, or by some other suitable means.

A sharp distinction must be drawn between the Bessemer and the Thomas-Gilchrist processes, although the apparatus and

manner of conducting the processes are almost identical. In the former no elimination of phosphorus from the pig-iron is possible, because the lining of the converter is very silicious, and any phosphates that might be formed would be at once reduced again. The use of calcined dolomite as a lining for the Thomas-Gilchrist converters, and of a quantity of basic material (lime) at the beginning of the blow, facilitates the absorption into the slag of any phosphoric acid that is formed by the oxidation of the iron phosphides in the charge. The phosphorus being thus fixed in the slag as a difficultly-reducible calcium phosphate, the iron is permanently dephosphorised. Both these processes yield ingot iron or ingot steel.

An attempt has been made to utilise the electric current in this process. According to Wikström[*] the iron is not sufficiently fluid after the Bessemer blow. He therefore proposes to attach to the blast-furnace a lander, so constructed that the stream of metal flowing through it is placed in the circuit of a powerful electric current. As it thus forms a resistance it becomes strongly heated, and at the same time air for the oxidation of the impurities is forced through it by means of a series of tuyères placed in the sides of the lander below the surface of the iron. The proposal, however, has so little prospect of success that no further discussion is necessary.

(e) The Siemens-Martin Process.—Pig iron is melted, together with malleable-iron scrap and with pure iron ore, in a Siemens regenerative gas furnace. The scrap serves, so to speak, to dilute the impurities in the pig iron, whilst the oxides on the surface of the scrap, together with the added oxide of iron in the ore, and aided by atmospheric oxygen, cause the oxidation of the constituents to be eliminated from the iron, and lead to their removal in the waste gases of the furnace or in the slag. This process, like that last described, may be either "acid" or "basic" in character, according to the nature of the furnace lining, and therefore of the reactions. The recarburisation of the molten charge, and deoxidation which is necessary, are effected by the means already mentioned so frequently. The last traces of ferrous oxide dissolved in the finished iron may be decomposed by the addition of a small quantity of aluminium. This process also produces ingot iron or ingot steel.

The use of electricity as a heating agent in the Siemens-Martin process has been protected by Taussig[†] in a number of patents. A hearth is constructed in which the metal to be refined, or the ore to be reduced, is introduced as a resistance in a powerful electric circuit, and is thus heated in the absence of air. But the steel metallurgist could have no difficulty in estimating the

[*] German Patent 76,604, Nov. 24, 1893.
[†] Nernst-Borchers, *Jahrbuch der Electrochemie*, 1894.

practical value of this process for foundry work or for refining, at least as it is described in various publications.

(*f*) **Annealing of Cast Iron.**—When objects are cast from white cast iron, and are heated for several days to a red heat, packed in red hæmatite, Fe_2O_3, or in chalybite, $FeCO_3$, they become so far decarburised as to be malleable. Probably the carbonic acid from the heating gases, or from the spathic ore, by diffusing into the metal acts as a decarburising agent; the CO_2 is reduced to CO by the carbon of the iron, and diffusing out again the latter oxide is oxidised to CO_2 at the expense of the oxygen of the ore. [It must be remarked, however, that in the treatment of large pieces of iron the bulk of the carbon is not actually oxidised, but is separated in the graphitic state in the midst of the iron itself, which thus has a peculiar greyish-black fracture after treatment.—TRANSLATOR.]

The electrical heating of the objects to be annealed has been proposed, but has not been satisfactorily accomplished.

(*g*) **Cementation.**—This is a recarburising process, and is, therefore, the reverse of [one form of] the "annealing," as described in the last paragraph. Malleable iron is packed in powdered wood-charcoal, and is thus heated for about a week to a temperature of 1000° C., and so becomes harder and stronger. Possibly the carbonic oxide produced by the action of the furnace gases upon the charcoal diffuses into the metal, and, dissociating according to the equation, $2CO = C + CO_2$, thus carburises it. [There is evidence, however, that iron may take up carbon by direct contact, and that the process depends largely upon this action.—TRANSLATOR.]

In the cementation process, especially if it be desired to produce steel of some definite grade of hardness, the electric current would appear to have some prospect of success, not only as a source of heat, but by hastening the absorption of the carbon. Reference can here be given only to the results of the carefully-conducted experiments by Hillairet and Garnier.[*] A carbon pencil and an iron rod (containing 0·1 per cent. C.) were so rested in a tube of refractory material that the ends of the two rods were in contact in the centre of the tube. The whole arrangement was heated in a small wind furnace. During the heating a current of 55 amperes × 7 volts was passed through the carbon to the iron, and then through the latter. After three hours of this treatment the iron was rapidly withdrawn from the apparatus and quenched in water. That end of the bar which had been in contact with the carbon was thus rendered so hard to the depth of 0·4 in. that it was capable of scratching glass. The surface of the carbon was found to be slightly roughened at the plane of contact. In order to prove that the carbon was actually conveyed into the iron by an electrolytic

[*] *Engineering and Mining Journal* (New York), 1894, vol. lvii., p. 57.

action, two iron rods were placed end to end, but separated by a piece of wood-charcoal 0·4 in. thick. The whole was then heated in the same manner as before, and to the same temperature (900° to 1000° C.), a current of 50 amperes × 2·5 volts being passed through the rods. After heating thus for three hours it was found that the iron rod which had served as anode remained practically unchanged, and scarcely became hardened on quenching, while the carburisation of the cathode iron had taken place to a considerable depth, and incipient fusion was observable at the lower end of this bar. Garnier thus demonstrates that the conversion of iron into steel may be hastened by the application of a weak electric current (50 amperes × 2·5 volts). But this statement, at least as far as it concerns the current strength, can only apply to objects of the dimension adopted in the experiment. The figures necessary for the determination of the current density are not available, although that is a matter of the highest importance.

So far as the absorption of carbon is concerned, this phenomenon is evidently comparable with liquid electrolysis, although in this case only solid substances are brought into play, so that the possibility of hastening cementation by the help of electricity is clearly beyond question. Electric cementation has, of course, been made the subject of many patents. The apparatus patented in this connection is for the most part crude, and not such as might be expected of arrangements that were considered worthy of protection by patent.

It will have become evident that, in spite of numerous published statements, the prospects of applying electricity to the production of cast or malleable iron are not as yet hopeful. Even the process last described requires that the objects to be treated should be comparatively uniform in dimensions.

THE WORKING OF IRON.

Thomson's Electric Welding Process.—It would seem that a more promising field for the application of electricity is to be found in the working of iron, and chiefly in the heating of iron prior to welding or soldering, or for smith-work and repairs. Space only permits of an outline account of the principles of the methods that have so far been described.

The first of these processes was applied chiefly to welding, and the object to be heated was placed as a resistance in the circuit of an electric current of such strength that the current density (current strength : cross-sectional area of object) was considerably greater than would correspond to its normal conductance. The well-known welding process of Elihu Thomson [*] is based, for example, on this principle.

[*] U.S.A. Patent 375,022, Dec. 20, 1887.

Two iron bars are pressed together with the aid of metal clamps, which at the same time form the poles of a powerful electric current, so that their ends are in contact as shown in Fig. 180. If the end surfaces are not true, it is evident that the bars can only touch at a comparatively few points, and the area of surface contact will therefore be much less than that of the rest of the bar, so that the resistance at this point will be higher in proportion. Further, this resistance is increased by the presence of a thin film of oxide on the surfaces of the metal. The temperature at the point of contact thus increases rapidly, and as soon as a welding temperature is reached, the bars are
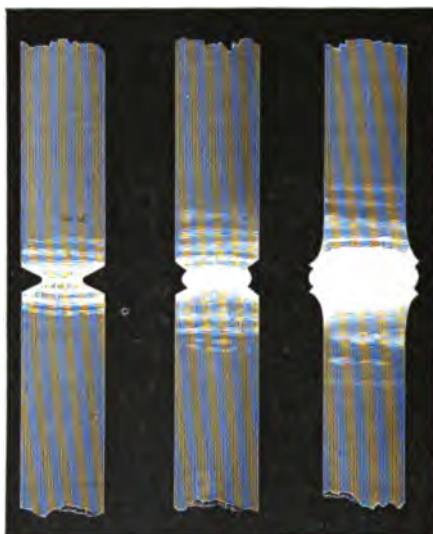
Fig. 180.   Fig. 181.   Fig. 182.

Elihu Thomson electric welding process.

pressed quickly together. The various stages in the heating are shown in Figs. 180, 181, and 182; but the application of the process is not, of course, confined to straight bars. The opinions of metallurgists are divided as to the value of this system, for the strength of the iron at the [unhammered] weld is neither very trustworthy nor very uniform. A current of low E.M.F., but of considerable volume, is necessary to heat the object in this way. It should amount to about 15 amperes * per sq. mm.

* [A bar of steel of 1 sq. in. sectional area should absorb the equivalent of 22 H.P. for one minute. Smaller bars would require less time (down to a few seconds) but a proportionately higher expenditure of energy, whilst larger bars would absorb less power but would need more time, up to about two or three minutes for a 2-inch bar.—TRANSLATOR.]

[10,000 amp. per sq. in.] of sectional area of the object to be welded in the immediate neighbourhood of the joint. The same process is recommended for the heating of wires or rods, the wire being drawn over the two ends of an interrupted electric circuit in such a manner that it makes contact, and so forms a resistance between them. Since single wires may be heated in this fashion, there is no doubt that whole bundles or packets might be similarly raised to a temperature suitable for rolling, and the re-heating furnace may possibly be even replaced under certain circumstances by an electrical heating plant.

Local Softening of Quenched Steel.—The melting of cast-iron for foundry work by the resistance heating method has not advanced to the practical stage, even though isolated reports of a not unfavourable character have been published concerning the Taussig smelting furnace to which allusion has been made above. One of the latest applications of this method of heating is to be found in the local softening of armour plates which have been superficially hardened by Harveyising; this may be required if extra rivet holes should be required at the last moment to secure the plates to the hull of the ship, or if the plates have to be sub-jected to some special treatment. In order to effect this two parallel copper contact pieces 5 sq. cm. [$\frac{3}{4}$ sq. in.] in cross-section and 25 mm. [1 in.] apart are caused to lead a sufficient current to the part that is to be heated. A dull red heat will shortly be observed in the iron between the contacts. From this moment the current strength is gradually reduced, so that after about ten minutes the heated part will have been cooled below the critical hardening temperature, after which no hardening is possible on the removal of the contact.

[A detailed account* of a plant supplied by the Thomson Welding Company for the local annealing of the Harveyised armour plates of the "Oregon" (U.S. Navy) has recently been published. A 55 H.P. engine is used to drive a 40 kilowatt alternating dynamo, wound for an outturn of 135 amperes × 300 volts, when run at 1000 revolutions per minute. The exciter (a D-type, shunt-wound generator of 110 volts at 2000 revolutions) is drawn by a pulley on the armature shaft, and is connected with the field magnet coils of the alternator through a regulat-ing rheostat with German silver coils. The main alternator current is led to the primary coil of a "shell" transformer (*i.e.*, one with the coils *enclosed* within a laminated iron shell); the secondary coil consists of a single U-shaped turn of cast copper, to the ends of which copper contact-pieces may be attached. These are of various sizes and shapes, according to the work to be done, and they are water-cooled (within) to prevent the heat from the annealing operation penetrating to the coils of the transformer. The transformer is so suspended

* *Iron Age*, August 29, 1895.

on trunnions that it may be turned at any angle, and thus brought to bear (if need be) upon any part of a plate that is already in position. In the actual process of annealing, the rheostat is so adjusted that the alternator current shall at first be of minimum strength, affording a current of about 3500 amperes and 4 volts from the transformer. The proper contact-pieces for the work in hand are attached to the latter, the distance between the pieces being about $1\frac{3}{4}$ in., if the hole that is ultimately to be drilled be required $\frac{7}{8}$ in. in diameter. The contact-pieces are then brought down upon the plate so that the spot to be annealed lies centrally between them and thus forms a part of the secondary circuit of the transformer. A slight humming sound is heard, and the steel begins to be heated ; the resistance of the rheostat must then be gradually reduced so that a (maximum) current of 6000 amperes may flow through the secondary circuit, including the portion of the plate between the contact-pieces. The steel becomes visibly red hot locally, and bulges somewhat owing to expansion caused by the irregularity of the heating. After about three minutes from starting it is sufficiently hot between the poles to char or ignite a pine stick held in contact with it. The current is then gradually reduced again to the minimum (3500 amps.), so that at least ten or twelve minutes are occupied in reducing the temperature below the point (a dull red heat) at which the metal could harden by chilling from contact with the mass of cool steel around. The current may then be broken, and the metal cooled more rapidly. The annealed portion will be elliptical in shape, the major axis of the ellipse being about 4 in., and the minor axis $2\frac{1}{2}$ in., under the above-named conditions.—TRANSLATOR.]

The Benardos Electric Welding Process. — Another method of heating objects for fusion or soldering consists in bringing them *into contact with the poles of an electric arc.* Metals were melted in this manner by Siemens more than sixteen years ago, as indicated on p. 131. Benardos [*] has ingeniously adapted this idea to the soldering, perforating, riveting, and repairing of metals. The work forms the negative pole,[†] and a carbon rod held in some form of movable handle is used as the positive pole (Fig. 183). While an arc plays between the carbon and the part of the metal to be heated, the latter may be locally raised to its melting point, so that the most varied soldering and melting work may thus be done. There are, however, certain difficulties which militate against the general use of the process. In the first place, the temperature of the arc is far too high for most metallurgical purposes, and it is scarcely capable of regulation. Again the transfer of

[*] German Patent 38,011.
[†] [The work is now made the positive pole, see next paragraph.— TRANSLATOR.]

carbon from the carbon electrode to the molten iron of the object being heated is unavoidable, for the formation of an electric arc is of the nature of electrolysis with a gaseous electrolyte. The solidified metal of the part that has been soldered is, therefore, nearly always harder and more brittle than the rest of the material. Hence it is possible that the process will have to be restricted to the repairing of cast iron objects.

[The Benardos process is in constant use at the Halesowen Works of Messrs. Lloyd & Lloyd, to whom the translator is indebted for the following information, as well as for the opportunity of personally inspecting the working of the installation. Three 150 - volt dynamos are employed to charge 1440 Benardos accumulators arranged in 24 groups

Fig. 183. — Benardos' method of electrical heating.

of 60 each. These cells are composed of lead plates so perforated as to expose a large surface of the metal, and are made without "paste"; they thus have to be "formed" in the same manner as the original Planté battery. This construction of cell is obviously necessary, on account of the intermittent nature of the welding operations, and of the sudden demand for large volumes of current to be applied for a short time. Should the renewal of any lead plates become necessary in the cells, the fresh electrodes may be introduced directly, and the process of "forming" is then accomplished without any special treatment. All the leads from the dynamos, batteries, and welders are brought into the switch room, and are so arranged that they may be joined up in any required manner; the instruments necessary to the measurement of any, or every, circuit being placed in the same room.

In the smithy, the metal to be welded may be connected up to the conductor from the switch room, but more usually the anvil upon which the work rests is so connected. The other electrode is L-shaped, and consists commonly of a stout carbon rod, about an inch in diameter, which forms the short limb of the L, and is gripped at the end of a long holder held in the hand, and joined up to the opposite conductor from the batteries. It is especially to be noted that the carbon is connected to the negative, and the work to the positive battery lead, and not *vice-versa* as described in the accounts of the original Benardos process. Hence there is no longer the danger of a partial carburisation of the metal by the anode carbon, to which allusion has been made in the text. The process may, of course, be applied to the welding of straight bars; but it is most useful and economical when employed for such purposes as the welding of flanges on to pipes that are required to stand high pressures, or for the

burning out of surface flaws in steel castings, or the like, and
making good the cavities thus produced by melting metal of
similar character into them.   There are obviously hundreds of
other applications, and among them may be noted the burning
of holes in tubes, &c., or the cutting of metal in any desired
manner.

In use, the object to be welded is placed on the anvil and
connected to the positive lead; the welder, holding a coloured
glass screen in the one hand to protect his eyes from the glare
of the arc,* and grasping the carbon holder in the other, touches
the carbon on the work and then immediately and very rapidly
withdraws it, so that an arc of suitable length is formed.   The
length of the arc used depends mainly upon the thickness of the
metal under treatment.   If very short the heat is not only too
concentrated, but too intense, and a thin plate might be fused
through almost instantaneously; and, even if a good joint were
made with such an arc, there would be a possibility that the
great (and purely local) contraction of the metal on cooling would
then cause it to crack.   There is no difficulty in obtaining an arc
6 ins. long, or more, with the aid of a powerful current, and the
heat would then be diffused over a larger area of metal, but the
cost would be needlessly high.   For the work usually undertaken,
the arc is preferably from 2 to $2\frac{1}{2}$ ins. in length.   Within a few
seconds from the start the portion of the metal upon which the
arc is playing is brought into a plastic semi-fused condition that
is most suitable for the welding operation.   If an ordinary bar
were to be welded the metal would be raised to the required
temperature, and hammered as usual.   In other cases (e.g., in
uniting a flange to a tube) the parts to be joined may be cut, so
that when placed in position there is a V-shaped groove between
them, a small block of metal ($\frac{1}{4}$ to $\frac{1}{2}$ in. cube) is then placed at
a convenient point in the groove, the arc is started and caused
to play upon this portion, so that the area surrounding the metal
block is raised to a welding heat, and the block itself is just
melted into a plastic condition, the arc is then broken and the
joint completed with a former.   Another block is then placed

* [The greatest caution must be observed in working with these large
electric arcs.   They should never be looked at, even from a considerable
distance, without using a screen consisting of several thicknesses of deep
ruby and orange glass.   The writer has on several occasions, when working
with an electric furnace, suffered slightly from the effects even of an inad-
vertent glance at the arc.   In more serious cases that have come within his
knowledge, the most intense pain and irritation of the eye were felt, com-
bined with a copious flow of tears.   These effects are not commonly felt at
the time, but only after the lapse of several hours; the pain may then,
however, be almost unendurable for hours.   If, for any reason, it be neces-
sary to approach the arc closely for any length of time, the screen should be
of sufficient size to protect the whole face, as the action of the arc is com-
parable with that of direct sunlight, causing sun-burn and peeling of the
skin.—TRANSLATOR.]

next to this, and the arc re-formed, and the joint made in the same way. These operations are alternated, so that the weld is extended about 1 to 2 in. each time until the whole is complete. In boring or cutting a pipe, or other object, the arc is caused to play sharply upon one point until a complete perforation is made, and this is extended in either direction by altering the position of the arc. In filling up cavities the metal is built up little by little, after the manner explained above in the case of the long weld.

At Messrs. Lloyd's works the current pressure used averages 110 to 120 volts, while the volume is varied by the introduction of resistances, according to the work in hand. Speaking generally, the current employed for welding metal $\frac{1}{4}$ in. thick may conveniently be about 200 amperes, for metal $\frac{3}{8}$ in. thick about 250 amperes, and for $\frac{1}{2}$ in. thick 300 amperes. For steel castings, it might range from 200 to 500 amperes. It is evident that the volume of current may vary within wide limits, and somewhat smaller currents may be used for a longer time, but generally with less economy. Thus, in the welding of $\frac{1}{4}$ to $\frac{1}{2}$ in. metal, the current would range from 23,000 to 35,000 watts, which is equivalent to an absorption of 31 to 46 electrical H.P.—TRANSLATOR.]

The Slavianoff Process.—The process of Slavianoff, which depends upon the same principle as that of Benardos, can also be applied to the repair of cast goods for like reasons.

This inventor has substituted a metal electrode for the carbon pole employed under the other system. It is evident that such an electrode must fuse, and will then be liable to run into the faulty places of the latter; it should, therefore, be composed of the same material as the metal to be repaired. It is true that there is no danger in this case that an excess of carbon shall be taken up by the iron surfaces to be united, but the operation itself requires more care and skill than that of Benardos on the part of the workman, for if the metal melt off too rapidly from the positive electrode, the arc will be subject to constant fluctuation. On the one hand, there is always danger of short circuits being formed, but, on the other hand, the breaking of the arc has equally to be avoided. [A current of about 4,800 to 5,200 amps. per sq. in. of sectional area of bar is used at a pressure of 50 to 70 volts. —TRANSLATOR.]

The Lagrange and Hoho System.—Lagrange and Hoho also cause the object to form the negative pole of an electric arc, as in the processes last described; but this arc is produced (and the whole object is immersed) in an atmosphere of hydrogen produced by the electrolysis of an aqueous solution. A leaden vessel, or a lead-lined wood or stoneware tank, or else leaden plates of the greatest possible area, placed in a suitable receiver, serve as anode, whilst the objects to be heated form the cathode and present a relatively small surface (Figs. 184 and 185). The

electrolyte consists of an aqueous solution of sulphuric acid, or
of such salts as sodium or potassium carbonate or borax.   With
a sufficiently high E.M.F. (at least 110 volts), an electric arc is
formed (as a result of the high current density) between the
cathode and the electrolyte across the layer of hydrogen in which
the cathode is enveloped.   The object to be treated is thus
heated very rapidly, and is protected from burning by the
hydrogen surrounding it.   The process has been recommended
for the heating of rivets, of iron rods for smith work, or of horse-
shoes; or for the annealing of wires and analogous purposes.
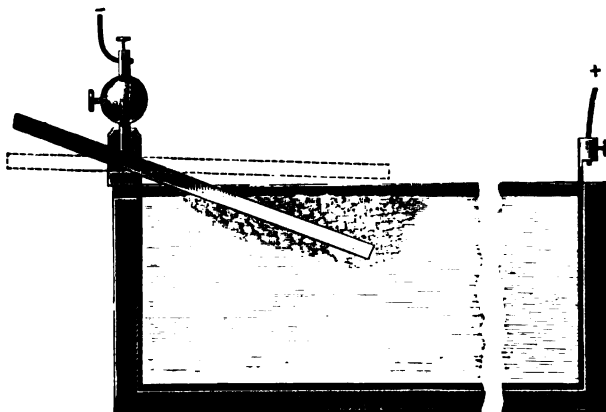
Fig. 184.—Lagrange and Hoho electrical heating method.
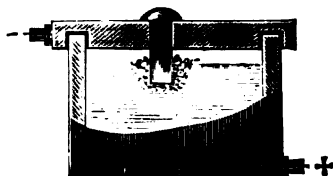
Fig. 185.—Lagrange and Hoho electrical heating method.

This process can only be used for the heating of objects that are
subsequently to be welded or hot worked, and during the heating
they are most efficiently protected from oxidation by the atmo-
sphere of hydrogen.   The Lagrange-Hoho apparatus has been
termed an electrolytic forge.   The condition of success for this
process lies in the treatment of small objects of uniform section.

[The Burton Liquid Forge.—In the process last described,
the hydrogen evolved is not utilised, except as an insulating
medium that enables an arc to be formed between the metal and
the liquid in which it is immersed.   Hence the 69,000 (gramme-
calorie) heat units absorbed in the electrolysis of each molecule

of water are wasted, when by burning the gas under suitable conditions, a considerable percentage might be recovered. To obviate this loss, G. D. Burton * has modified the apparatus in such a way that the specimen to be heated is merely brought into contact with the surface of the electrolyte; and the local heat of the arc thus formed is supplemented by that resulting from the combustion of the hydrogen produced. This process has been employed in the Niagara district. In its simplest form the forge consists of a tank, constructed of, or lined with, some non-conducting substance, and divided into three compartments by two perforated non-conducting partitions, one of which is placed transversely at one end, and one longitudinally near one side. In one is a leaden plate, which serves as anode, in another is a plunger, that may be raised or lowered to control the level of the liquid in the whole tank by displacement, while the third forms the "hearth." In the last named cell, the objects to be treated are introduced, either held in tongs connected with the negative lead from the dynamo, or supported on movable blocks of fireclay, the distance between which may be regulated at will. The latter method is used when only a portion of the object has to be raised to a welding temperature; connection with the current is then made by a clamp, and the space between the fireclay blocks regulates the length that will be heated. The electrolyte for small work may be a sodium chloride solution of 1·05 specific gravity, the density of which would be increased in proportion to the size of the work. An alternative solution contains 10 lbs. of washing soda, and 1½ lb. of borax to 45 gallons of water. As soon as the piece is placed in position, the operation may be started by depressing the plunger, and thus raising the level of the liquid until it just touches the object. A bar of iron, ¼ in. square, requires about 8 seconds, and a bar, 1 in. square, about 1 minute, to bring it to a welding heat, and the current in the latter case would average 26 amp. × 220 volts. The current is passed continuously in treating small bars; but for irregular pieces, it is advisable to render it intermittent, in order that the heat may have time to become equalised throughout the metal, instead of being concentrated at one point. The hydrogen evolved by the electrolysis escapes into the air, and there, igniting by contact with the arc, forms a flame which envelopes the bar and assists the heat from the arc in raising it to the required temperature.—TRANSLATOR.]

The Zerener Process.—Zerener,† in his soldering process,

* [English Patents 7712, 7713, April 17, 1895; and *Electrical Engineer* (New York), 1895, p. 93.]

† [Zerener in the *Sitzungsberichte des Vereins zur Beförderung des Gewerbefleisses*, 1893, p. 211, states that with the hand tool, bicycle frames and the like may be brazed with the aid of a current of 40 to 60 amp. × 40 volts, and that with the larger instrument an iron plate ¼ in. thick may be welded by a current of 100 to 200 amp. × 70 volts.—TRANSLATOR.]

heats the objects in the electric arc, but without making them electrodes. The difficulties militating against the practical application of this method have been overcome by placing the carbon electrodes opposite to one another in a slanting position, and deflecting the arc that plays between them by means of an electro-magnet placed at right angles to the plane of the arc. Fig. 186 is a diagrammatic sketch of such an arrangement. K K are the carbon electrodes, M M is the electro-magnet actuated by the main current passing through a coil of a few turns of wire, the poles being placed at right angles to the plane of the electrodes. The arc is deflected downwards like the flame of a blow-pipe. [This principle was also applied to electric furnaces in 1886 by Rogerson-Statter and Stevenson.—TRANSLATOR.] The smallest forms of the apparatus are fitted with handles, so that they may be used like a copper bit or a brazier's blowpipe; the larger forms must be mounted like a small crane. It is evident that most of the difficulties encountered in the use of the electric soldering and welding apparatus previously described have here been surmounted. The arc is independent of the object under treatment; and by altering the distance between them, the temperature may be kept under perfect control; whilst a smaller current suffices for the work.

Fig. 186.—Zerener's Apparatus.

The current may vary between 3 and 250 amperes at a pressure of 60 to 65 volts, according to the size of the apparatus. Hence the system may be adopted wherever a current is used for electric lighting, while for the other systems an installation of accumulators is necessary. In short, everything appears to indicate that of all the hitherto known methods and apparatus for working metals by electrical means, that of Zerener is likely to find the most extended use.

The iron industry has utilised electricity in a manner somewhat different from that of the other branches of metallurgy. Without being of practical service in the reduction and refining of iron, electricity has been employed in the preparation of the raw material, and in the treatment of the finished metal.

In conclusion, however, it may be again urged that in the centres of the iron industry, the waste of chemical energy is simply stupendous. There are many ironworks in which gases from the blast furnaces and coke-ovens are allowed constantly to go to waste, that would be capable of developing thousands of H.P. units. Even the crudest steam-engine plant imaginable

could here be made to generate electricity and drive an electric installation with profit, seeing that the power could be had practically for nothing.* Instead of this, even the most remote sources of water power are sought out for the operation of electrolytic processes; whilst in the most flourishing industrial centres the power is scattered to the winds to an extent that in other countries would suffice to attract a valuable electro-chemical industry. It is to be hoped that the recognition of this error will soon become general; and none will be found to begrudge to the iron works the premier position in the field of electrometallurgy.

CHAPTER XII.

NICKEL AND COBALT.

Properties of Nickel.—Nickel (Ni; atomic weight = 58·88; specific gravity = 9) is a very clear grey, and brilliantly lustrous metal, distinguished by its tenacity and malleability, which are so high that, like iron, it may be rolled or drawn to sheet or wire. In its magnetic and electrical properties it strongly resembles iron. The melting point of nickel is about 1400° C. It alloys readily with most metals (cupro-nickel, copper-zinc and nickel, German silver, ferro-nickel, nickel steel). Like copper and iron, melted nickel is capable of dissolving some of its own compounds, as, for example, the oxide. At ordinary, and even at comparatively high, temperatures nickel oxidises but slightly in the air, so that the waste in the form of scale produced in rolling, or in hot working, is much less than in the case of iron. It combines readily with the metalloids, and its compounds with sulphur and arsenic play an important part in the metallurgy of the metal. All the more important nickel compounds met with industrially are derived from the protoxide, NiO; the peroxide being a very unstable body. Nickel dissolves readily in nitric acid, and more slowly in hydrochloric or sulphuric acid, and forms the salts of the protoxide in each instance.

Occurrence of Nickel.—Nickel occurs only in the form of sulphides or arsenides, or their weathering products, and as silicate. The two first-named are found, for the most part, accompanying the corresponding compounds of copper and iron, and

* [Successful experiments have recently been made by Dixon and Thwaite at the Wishaw works of the Glasgow Iron and Steel Co., in the direct use of the blast furnace gases in gas engines. These have at present shown that 78·54 cb. ft. of gas per hour may suffice to generate 1 H.P. (indicated), or 105 cb. ft. to give 1 H.P. (actual).—TRANSLATOR.]

they formed until recently the most important nickel ores. But lately the silicates, and among these garnierite, have been abundantly smelted.

Extraction of Nickel.—The extraction of nickel is almost exclusively effected by processes conducted on the lines of those employed for the treatment of copper or iron ores. For example, there are concentration processes for nickel exactly similar to the smelting for matte in the metallurgy of copper. With arsenical ores a system of speise-smelting may be substituted for matte production, and, if necessary, the speise, like the mattes, may be roasted, and then submitted to a second fusion. Even the silicates may be smelted with sulphide ores, so that a nickel matte may be formed which is then treated like the corresponding copper product and made to yield a crude nickel. The crude nickel may then be refined by a process similar to that employed for the conversion of cast into wrought iron; and for this purpose the principles of the puddling, the Bessemer, and the open-hearth processes have been borrowed from the metallurgy of iron. It is, however, necessary to use powerful reducing agents to decompose the last traces of nickel oxide in metal which has been refined by oxidisation; and magnesium was found by Fleitmann to give the most satisfactory result. [The principle of the Burton forge (see p. 390) is said to have been applied to the treatment of nickel ore in Canada, the ore (presumably oxide) being enclosed in a cradle and submitted to the combined action of the arc and of hydrogen by immersion as the positive electrode to a current of great density in a suitable electrolyte.—TRANSLATOR.]

When the ores contain cobalt the smelting is supplemented by so-called "wet-processes." After smelting for matte or speise, and roasting the product, the resulting oxides are dissolved in acid; the salt solution is treated with hydrogen sulphide to precipitate copper, lead, and certain other metals. The filtrate from the sulphides is first neutralised and then oxidised by chloride of lime, so that the iron becomes precipitated as ferric hydroxide, and afterwards the cobalt is deposited as peroxide. The nickel is finally precipitated as nickelous hydroxide from the separated solution, and thus is dried and reduced to the metallic state.

Mond's process is still in the experimental stage; it consists in converting the nickel of oxidised ores into nickel carbonyl, $Ni(CO)_4$, with the aid of carbonic oxide; the carbonyl passes off as a gas, and is dissociated again, by heating, into metallic nickel and carbonic oxide.

So, also, the electrolytic extraction of nickel is still under experiment, and it yet remains to be ascertained whether it can ever be applied on the large scale. It is somewhat strange that a metal, which, in electro-plating, gives sound, adhesive

and brilliantly lustrous thin films, should cause so much trouble as soon as it is sought to obtain a deposit of any considerable thickness.* Processes for electro-nickeling have been known for upwards of half a century; but even the simplest problem in the electrolytic refining of nickel has not yet been satisfactorily solved. Some of the proposals in this direction may be shortly reviewed.

The possibility of depositing nickel by electrolysis does not appear to have been contemplated before 1840. But there then appeared an English patent which protected the use of double cyanides as an electrolyte in the deposition of nickel, a method well known at the time to be suitable for the electrolysis of many other metals. This process, however, has been of no service in the electro-metallurgical extraction of nickel. From a practical point of view, R. Böttger's experiments † were of much greater importance, for they showed that nickel could be obtained as a lustrous, silvery white, thin deposit from solutions of the double sulphate of nickel and ammonium. Reference will be made hereafter to developments of this process.

André's Process.—The first specification relating to the extraction of nickel originated with E. André,‡ who proposed that "nickel-mattes, speise, or impure nickel-cobalt and copper compounds should be connected with the positive pole of a generator, and be suspended as anodes in dilute sulphuric acid. Copper or carbon plates are used as cathodes to receive the deposit of pure copper, for the nickel passing into the solution is not deposited so long as the electrolyte is acid. In order to separate every trace of copper from the solution, a carbon plate is substituted towards the end of the operation for the matte or alloy employed as the positive pole. The copper is then deposited very rapidly by the current, so that there remains a weak acid solution of nickel sulphate containing a little iron. A small quantity of ammonia is then added to the solution, and air is passed through it whilst it is being evaporated in leaden pans. The iron is thus separated as the flocculent hydroxide, and is removed either by sedimentation or by filtration. Pure nickel sulphate could then be obtained from the solution by concentration.

"In order to recover metallic nickel from this solution, the iron is first removed in the manner indicated, and then the nickel is deposited on carbon, nickel, or black-leaded copper anodes, the

* [The electro-deposition of thick plates of nickel has, however, been successfully carried on for some time by Messrs. Thomas Bolton & Sons, of Cheadle, who are using nearly neutral solutions, in England, and by the Balbach Smelting and Refining Co. in New Jersey, who have been engaged in refining nickel anodes containing about 95 per cent. of nickel. But the details of the processes in use have not yet transpired.—TRANSLATOR].

† *Journal für praktische Chemie*, vol. xxx.; p. 267.

‡ German Patent 6048, Nov. 1, 1877.

solution having first been made ammoniacal. Carbon or platinum anodes cannot be used, because the current from the dynamo would then be rapidly diminished by polarisation; iron or zinc should therefore be employed, but as these dissolve under the influence of the current, the positive and negative electrodes must be separated by a double membrane, and the liquid between the two membranes must be drawn off from time to time to prevent the mixing of the iron (or zinc) sulphate solution formed at the anode with the nickel solution. In this manner the nickel ores of New Caledonia may be made to yield pure nickel from their solution in sulphuric or hydrochloric acid.

"By suspending the matte, speise, or the like as anodes in an ammoniacal bath, copper and nickel are deposited simultaneously, and this alloy can be treated again after its removal from the carbon plates."

The impression produced by this specification is not very satisfactory. In the first place the iron is to be removed with great care, and yet the use of iron anodes is recommended. There is no fear of iron dissolving in ammoniacal solutions, for under these circumstances the iron plates become rapidly covered with a film of ferric oxide, but the electrolyte remains almost free from iron, provided it is kept ammoniacal. At the same time there will very soon be left no iron anode capable of being oxidised and therefore of acting as a depolarising agent; but in its place there will be an anode of the completely inactive ferric oxide, which cannot serve as a depolariser. Zinc may be employed instead of iron, and as it dissolves in the electrolyte depolarisation is ensured. So expensive an agent as the electric current would generally be used in refining only to ensure the production of a pure metal, but it has so far been found impossible to obtain a deposit of pure nickel from solutions which contain more than a mere trace of zinc.

Farmer's Process.—Some ten years later, Farmer[*] patented in America an apparatus which was to be used in the production of nickel plate. In Figs. 187 and 188, A A are tanks, such as are commonly used for the electro-deposition of metals. In the upper part of these vessels are rollers, B, made of wood, stone, or other non-conducting substance, provided with coverings of canvas or similar material, so arranged that the rollers may be easily withdrawn from them. These rollers serve to maintain the open-ended hollow cylinders, E, in continuous slow rotation. The cylinders are made of brass or copper, and serve as cathodes; they are kept from lateral motion by the flanges, C, C', attached to the rollers. The nickel plates, E', are bent into half-cylinders, and are used as anodes. The metal arm, F, which is free to turn about an elbow joint in a vertical plane, carries a roller, D (also made of conducting material, and mounted on c), by which the

[*] U.S.A. Patent 381,004, April 10, 1888.

cylinder, E, is pressed into contact with the rollers, B B, and is connected with the negative pole of the electric generator.

During electrolysis the tanks are filled with a nickel solution to the level shown in the figures, the double sulphate or nitrate of nickel and ammonium being recommended for the purpose. The current enters by the anode, E', of the apparatus on the right, and passes through the electrolyte to the cylinder, E, which makes one revolution in the minute, the motion being derived from the rollers, B B, rotated by means of the pulley, P. From the cylinder, E, the current passes through the roller, D, and the arm, F, to a wire which conducts it to the next bath;
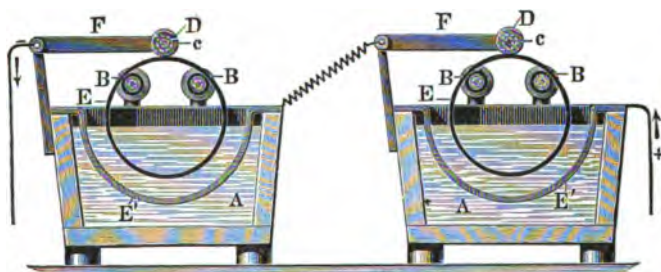
Fig. 187.—Farmer's nickel depositing plant (longitudinal section).
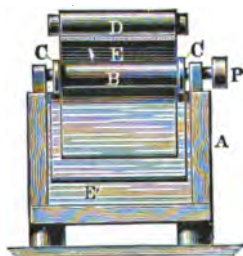
Fig. 188.—Farmer's nickel depositing plant (cross-section).

and thence it returns to the opposite pole of the generator, either immediately or after passing through one or more other tanks.

If the object of the apparatus were merely the alteration in the outward shape of metals (especially of nickel), the means would be found very expensive, and would not be likely to displace older and well-tried methods. A combination of metal refining with the production of articles of some special shape, such as tubes or plates, is conceivable, but no mention is made of such an intention, nor would it be of any service at present in the treatment of nickel. The metallic impurities of nickel cannot well be separated by purely electrical means, at least, if the nickel is to be obtained in the metallic condition in the

same operation. With the current density that is necessary for the deposition of nickel nearly all metallic impurities would also be separated.

The Basse-Selve Process.—The firm of Basse and Selve* have patented a process for the separation of nickel from iron, cobalt, and zinc in a solution containing salts of all these substances. The neutral or slightly acid aqueous solution of iron, zinc, or cobalt, together with the nickel salt, is first mixed with a sufficient quantity of an organic compound that is able to prevent the precipitation of ferrous, or ferric, oxide, zinc oxide, or cobaltous, or nickelous, oxide, by the addition of alkalies; a concentrated solution of caustic potash or soda is then added in moderate excess, and the mixture is submitted to electrolysis.

With a current of 0·3 to 1·0 ampere (? per sq. decimetre) iron, cobalt, and zinc separate at the cathode. The nickel either remains in solution, or (especially by long-continued electrolysis) separates in part as hydroxide, according to the concentration of the alkaline liquid. When the solution is very alkaline and the electric current is moderately strong (1 ampere or over), a small proportion of the nickel separates out as black oxide on the anode; but this black deposit vanishes if it be left for some time in contact with the alkaline organic liquid after the current has been broken.

To obtain the nickel in the metallic condition, the alkaline solution, from which the iron, cobalt, and zinc have been removed, is mixed with sufficient ammonium carbonate to convert all free caustic alkali into carbonate, and it is then electrolysed. It is not necessary for the electrolytic separation of iron, cobalt, and zinc that the nickel oxide should be dissolved in the electrolyte; it is sufficient that the metals to be separated should be entirely dissolved, and the nickel may then be present in the form of precipitated nickelous hydroxide.

Either tartaric or citric acid, glycerine, dextrose, or other organic compounds may be employed to retain the metals in solution in presence of free alkali, but the first named affords the most satisfactory separation.

The Hoepfner Process.—Hoepfner† prepares, in the first place, a purified neutral solution of nickel by any known method; this is then acidified with a weak and feebly-conductant oxygen acid (e.g., citric or phosphoric acid), and is electrolysed with the aid of insoluble anodes. The anodes are immersed in cells containing a solution of the chlorides of more electro-positive metals. Vertically-mounted, rotating or oscillating plates serve as cathodes. The formation of spongy masses is prevented by the application of movable brushes or pads, and the electrolyte is kept in brisk motion by means of pumps.

* German Patent, 64,251, Dec. 22, 1891.
† English Patent 13,336, 1893.

The anodes may be made of some metal that is partly or wholly soluble in the solution, in place of those recommended, but in that case some more electro-positive metal (zinc), which will not be deposited with the nickel, must be used.

It is proposed to adapt the same method to the separation of cobalt, zinc, lead, tin, or copper.

The Rickets Process.—Rickets'[*] process for the separation of nickel and copper does not appear to give great promise of success. It consists in electrolysing the salts of the two metals in solution after the addition of alkaline sulphates. While the copper is deposited on the cathode, and the solution becomes more acid in consequence, the nickel separates at the bottom of the vessel in the form of a nickel-alkali-metal sulphate, this salt being less and less soluble in the increasingly acid liquid.

Deposition of Pure Nickel and Cobalt. — Finally, the process[†] may be described by which Bischoff and Thiemann deposited the pure metal used by Cl. Winkler in his researches on the atomic weights of nickel and cobalt.

For the production of nickel, a solution of the purest nickel sulphate was used, containing 32·84 grm. of nickel per litre. The electrolyte prepared with this contained :—

> 200 c.c. nickel sulphate solution.
> 30 grm. ammonium sulphate.
> 50 grm. ammonia (of 0·905 sp. gr.).
> 250 c.c. water.

Since nickel deposited upon platinum is with difficulty detached from its surface, a highly polished nickel plate, 9·7 cm. long by 7·9 cm. wide, was, with advantage, used as cathode, whilst a platinum plate was opposed to it as anode. A dynamo was employed as generator, and a resistance was placed in the circuit, of such strength that a fall of potential of 2·8 volts corresponded to a current of 0·8 ampere. The current density was, therefore, $D_{100} = 0·5$ ampere. As soon as the nickel deposit had attained a certain thickness it began to peel spontaneously from the surface upon which it was depositing in thin, and more or less curled, flakes, and there was obtained 13·13 grm. of pure nickel in the course of 20 hours. The metal was white and lustrous, but, as compared with cobalt, showed a distinct tinge of yellow. No tarnish or specks of oxide were visible, and the metal showed no loss whatever when heated to redness in a current of dry hydrogen which had been previously purified by passing over a roll of red hot iron wire gauze. This proved that the electro-deposited nickel had been entirely metallic in character.

[*] U.S.A. Patent 514,276, Feb. 6, 1894.
[†] *Zeitschrift für anorganische Chemie*, vol. viii., 1895.

For the production of cobalt, a pure sulphate of cobalt, mixed with ammonium sulphate, was prepared by heating purpureo-cobaltic chloride with sulphuric acid. The aqueous solution of this contained 11·64 grm. of cobalt per litre; and the electrolyte was made up as follows :—

> 100 c.c. cobalt sulphate solution.
> 30 grm. ammonium sulphate.
> 30 grm. ammonia (of 0·905 sp. gr.).
> 500 c.c. water.

The cathode was a platinum plate 9·4 cm. long by 5·9 cm. wide, and a similar platinum plate served as anode. The strength of current was 0·7 ampere at 3 volts, and the current density $D_{100} = 0·6$ ampere. The deposited cobalt weighed 8·133 grm., of which 7·319 grm. separated from the cathode in the form of a coherent and fairly strong plate. The metal was brightly lustrous on the side next to the platinum, but on the other side it was dull and grey ; it was not tarnished, however, and showed but little oxide. On heating in pure oxygen it lost 0·23 per cent. in weight, so that it must have contained 0·55 per cent. of cobaltic oxide ($Co_2O_3 + 2H_2O$) ; in other words, 0·32 per cent. of the total weight of cobalt had been deposited as oxide.

In a second experiment, the electrolyte consisted of :—

> 250 c.c. cobalt solution.
> 30 grm. ammonium sulphate.
> 50 grm. ammonia (sp. gr. = 0·905).
> 250 c.c. water.

A polished nickel plate, 9 cm. long by 7·6 cm. wide, was used as cathode, and a platinum plate as anode. The current strength was 0·8 ampere at a pressure of 3·2 volts, and the current density was $D_{100} = 0·6$ ampere. The action was stopped after 30 hours, and afforded 2·9 grm. of metal, of which 2·2 grm. were easily separated from the cathode in the form of thin and curled frag-ments of plate. The metal so obtained was in parts perfectly lustrous, but in many places was flecked with brilliant tarnished spots, or tinged with brown. On heating in hydrogen, it lost 0·15 per cent. in weight, which corresponds to 0·36 per cent. of cobaltic oxide ($Co_2O_3 + 2H_2O$). Hence 0·21 per cent. of the whole of the cobalt had been deposited as oxide. The deter-minations of oxide made in this way, however, are likely to be a little too high, because the deposited metal retained traces of ammonium salts, even after very thorough washing ; and these were volatilised on heating in hydrogen, affording a slight brownish ring of deposit in the cooler part of the tube. After heating in hydrogen, the cobalt had a uniformly metallic appear-ance, and in parts formed plates with a beautiful lustre. Its colour, as compared with nickel, was distinctly bluish-white, like that of zinc.

Summary.—If one might judge solely from patent specifications, of which the best known have been more or less fully quoted here, the problem of extracting nickel by electrolysis on the commercial scale might be considered as solved. The methods that have been worked out for electrolytic analysis * show that nickel may be separated quantitatively in the form of a dense and lustrous deposit from quite a number of salts. Again, the processes are not less numerous by which a bright and adhesive coating of nickel may be deposited on the more important metals. The analyst and the electro-plater attain their respective objects with certainty, but no process of depositing nickel continuously for the industrial extraction of the metal has yet been made public.

Since the metallurgy of copper † has been taken as typical of that of nickel, it might at first seem possible that the crude nickel could be refined without difficulty after the manner of the electrolytic process for copper. It is, however, only necessary to call to mind the nature of the impurities in nickel to recognise that this process has no prospect of success. The objections to the direct electrolytic treatment of nickel ore and matte will be understood on reference to the account of analogous processes in connection with copper extraction.

There remain only the wet processes for the treatment of the nickel ores, which permit the electrolytic precipitation of the nickel after the bulk of the impurities has been removed from the solution by precipitation. But the conditions necessary for such are:—

The best electrolyte is the sulphate, and although on the one hand it may with advantage exhibit an acid reaction, yet on the other hand it must not contain any of the mineral acids in the free condition. Boric and phosphoric acids, however, appear to be harmless. Of basic solutions only those which are ammoniacal can be used.

The unsatisfactory character and the cost of working with insoluble, but yet not indestructible, anodes have been sufficiently explained already.

Under these circumstances an E.M.F. of 3 volts must be applied to obtain a current density of 60 to 100 amperes per sq. metre [0·04 to 0·65 amp. per sq. in.]; and it is only when depolarising agents, such as organic acids, are present that the difference of potential may be reduced to 2 to 2·5 volts. Among the organic acids that are good conductors, and of which the price is not prohibitive, the author has already recommended ‡ the use of the sulphonic acids of the less valuable distillation products of tar.

* A. Classen, *Quantitative Analyse durch Elektrolyse*, 3rd. Ed., 1892.
† G. Langbein, *Galvanische Metallniederschläge*, 3rd. Ed., 1895.
‡ See Chapters on *Lead* and *Zinc*.

Although there is no longer any difficulty in producing thin deposits of nickel which leave nothing to be desired in respect of soundness, lustre, and colour, it has not yet been found possible even with the greatest care, to obtain thicker plates that could be subjected direct to mechanical working.   Even in nickel-plating, if an extra thick coating be required, it is necessary to stop the process after a certain thickness of nickel has been deposited, and to coat this with a thin film of copper before proceeding further.   Only in this way will the nickel coating be adhesive, for electro-deposited nickel shows a tendency to break away, and to flake off as the thickness is increased.   It may be that the cause of this is to be ascribed to the formation of an almost imperceptible film of oxide, as would seem possible from A. Winkler's experiments.   This, however, is only a conjecture, and no sufficiently inexpensive method of obviating the difficulty has yet been found.

Thus there is at present no publicly described electrolytic process which, at a sufficiently reasonable cost, can produce a metal that is capable of being worked mechanically.   And so long as the electro-deposited nickel has yet to be fused and refined subsequently, the commercial practicability of electro-lytic methods must be held in doubt.

The Applications of Nickel.—Pure nickel is used in con-siderable quantities for cooking and table utensils.   Nickeled-iron sheet, made by welding together nickel and iron plates, is employed for similar purposes.   Many objects in common use consist of a cheaper metal electro-plated with nickel.   Among the alloys may be included—cupro-nickel for coinage, &c., nickel-copper-zinc as German silver, &c., and nickel iron, such as nickel steel for armour plates.

Cobalt.—Excepting the method described above for the production of pure cobalt, it will not be necessary to enter into details of the treatment of this metal, inasmuch as nearly all that has been written concerning nickel is equally applicable to cobalt.

CHAPTER XIII.

METALS OF THE PLATINUM GROUP.

THERE is but little need to refer to this group of metals, since there is not much prospect of electrolytic methods of extraction being applied to them, owing to the fact that most of their com-pounds may be readily decomposed by a slight expenditure of heat.   Several methods of depositing and separating the metals

by electrolysis have been published during the last few years.
It should be stated, however, that these methods have been
mainly devised for purposes of analysis or electro-plating, and
may therefore be found described in such works as those of
Classen and Langbein, to which reference has been made so
frequently.*

A process for the separation of gold and platinum has already
deen described in the Chapter relating to the former metal.   In
a similar way by using a platinic chloride solution as electrolyte,
platinum may be separated from certain other metals (iridium
and rhodium) of this group.

The use of the Siemens electric furnace (see p. 131) for melting
platinum has not been successful owing to the readiness with
which the carbon of the electrode passes over into the platinum;
and platinum containing carbon is inapplicable to most purposes.
If platinum is to be melted by electrical means, it will be either
by placing the metal as a resistance in a powerful electric circuit,
or by causing the electric arc to pass to the metal from an elec-
trode of the same material, as Slavianoff has proposed for use in
the treatment of iron (see Chapter on *Iron*, p. 389).

* See also Translator's *Treatise on Electro-Metallurgy.*

ADDENDA.

TABLE I.—SHOWING THE VALUE OF EQUAL CURRENT VOLUMES AS EXPRESSED IN AMPERES PER SQUARE DECIMETRE, PER SQUARE FOOT, AND PER SQUARE INCH OF ELECTRODE SURFACE.

Amperes per Square Decimetre.	= Amperes per Square Foot.	= Amperes per Square Inch.	Amperes per Square Decimetre.	= Amperes per Square Foot.	= Amperes per Square Inch.	Amperes per Square Decimetre.	= Amperes per Square Foot.	= Amperes per Square Inch.
0·05	0·46	0·0032	0·8	7·43	0·0516	6·20	57·6	0·4
0·054	0·5	0·0035	0·86	8	0·0555	6·46	60	0·4167
0·077	0·72	0·005	0·9	8·36	0·0581	7	65·0	0·4516
0·1	0·93	0·0064	0·93	8·64	0·06	7·53	70	0·4861
0·11	1	0·0069	0·97	9	0·0625	7·75	72·0	0·5
0·15	1·44	0·01	1	9·29	0·0645	8	74·3	0·5161
0·2	1·86	0·0129	1·08	10	0·0694	8·61	80	0·5555
0·22	2	0·0139	1·09	10·08	0·07	9	83·6	0·5806
0·3	2·79	0·0193	1·24	11·52	0·08	9·30	86·4	0·6
0·31	2·88	0·02	1·39	12·96	0·09	9·69	90	0·6250
0·32	3	0·0208	1·55	14·4	0·1	10	92·9	0·6452
0·4	3·71	0·0258	2	18·6	0·1290	10·76	100	0·6944
0·43	4	0·0278	2·15	20	0·1389	10·85	100·8	0·7
0·46	4·32	0·03	3	27·9	0·1935	12·40	115·2	0·8
0·5	4·64	0·0323	3·10	28·8	0·2	13·95	129·6	0·9
0·54	5	0·0348	3·23	30	0·2083	15·50	144·0	1
0·6	5·57	0·0387	4	37·1	0·2581	20	185·8	1·2903
0·62	5·76	0·04	4·30	40	0·2778	21·53	200	1·3889
0·65	6	0·0417	4·60	43·2	0·3	30	278·7	1·9355
0·7	6·50	0·0452	5	46·4	0·3226	31·0	288	2
0·75	7	0·0486	5·38	50	0·3478	32·3	300	2·0833
0·77	7·20	0·05	6	55·7	0·3871	46·5	432·0	3

By this table the current density may be expressed in amperes per square decimetre, square foot, or square inch, any one of them being given. Thus a current of 1 ampere per square decimetre has the same electrolytic value as one of 9·29 amperes per square foot, or 0·0645 per square inch. To find the value of intermediate numbers not shown above, add together the various numbers representing the hundreds, tens, units, and decimals of the given quantity. Thus 27·5 amperes per square decimetre (= 20 + 7 + 0·5) is equivalent to 185·8 + 65 + 4·64 = 255·44 amperes per square foot, or 1·2903 + 0·4516 + 0·0323 = 1·7742 amperes per square inch.

Note.—This table is re-printed from the Translator's *Treatise on Electro-Metallurgy.*

TABLE II.

COMPARISON OF CENTIGRADE AND FAHRENHEIT THERMOMETER SCALES

Fah.	Cent.	Fah.	Cent.	Fah.	Cent.	Fah.	Cent.
Deg.	Deg.	Deg.	Deg.	Deg.	Deg.	Deg.	Deg.
32	0	752	400	1400	760	2000	1093
100	37·8	800	427	1472	800	2012	1100
200	93·3	842	450	1500	815	2102	1150
212	100	900	482	1562	850	2192	1200
300	149	932	500	1600	871	2372	1300
400	204	1000	538	1652	900	2552	1400
482	250	1022	550	1700	927	2732	1500
500	260	1100	593	1742	950	2912	1600
572	300	1112	600	1800	982	3092	1700
600	316	1202	650	1832	1000	3272	1800
662	350	1300	705	1900	1038	3452	1900
700	371	1382	750	1922	1050	3632	2000

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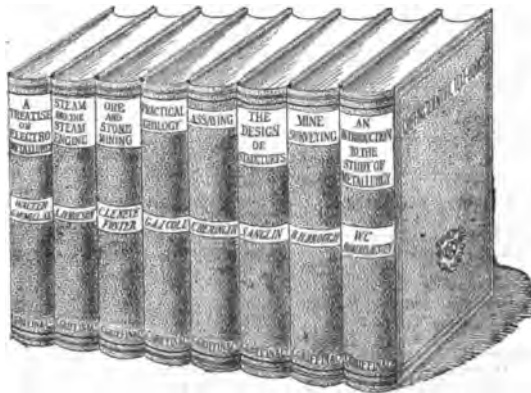
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